HIGH TEMPERATURE MATERIALS, INC.

130 LINCOLN STREET
BOSTON • MASSACHUSETTS

FINAL REPORT

on

Pyrolytic Carbide Development Program

March 15, 1960 through September 30, 1961

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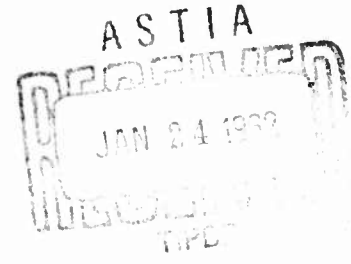

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ABSTRACT

Refractory pyrolytic carbides were investigated for use as erosion resistant barriers on the surface of rocket nozzles. The materials were developed specifically for application to Polaris nozzles where advanced propellants are contemplated.

A pyrolytic process utilizing a mixture of reactant gases composed of a metal halide and a hydrocarbon was developed for the production of coatings of tantalum carbide, hafnium carbide and niobium carbide on graphite substrates. High density, single phase, impervious carbide coatings were produced which are intimately bonded to their substrate. To produce crack free carbide coatings on graphite, special graphites are required which have coefficients of thermal expansion compatible with those of the carbides.

Pyrolytic TaC and NbC coated rocket nozzle inserts tested at the Atlantic Research Corporation were found to resist erosion. Partial failures in term of removal of the coatings in the exit cone section of the nozzles appeared to be due to thermal stresses or possibly from structural changes in the substrate material used. Thermal shock does not appear to be a problem, especially, when their coatings are employed.

The feasibility of producing full scale rocket nozzles with surface coatings of pyrolytic carbides was also demonstrated during the course of the program.

INTRODUCTION

The advances in rocket technology have progressed in a general way along two avenues which are intimately connected with material developments. One is the concentration on the use of solid propellants which are required in a number of cases for obvious reasons. Solid propellants contain constituents which increase the erosion of rocket nozzles and are therefore more demanding of nozzle materials. Since increases in propulsion efficiency go hand in hand with increases in operating temperatures, the higher flame temperatures presently attained and to be reached in the future restricts the selection of material to relatively few highly refractory materials. Second is the gain in simplification in the use of uncooled instead of cooled nozzle structures. Uncooled nozzles can attain higher operating temperatures but could be lighter weight structures which are required for optimum efficiency.

To satisfy the above requirements a material is needed which is extremely refractory, highly erosion resistant, chemically inert to the propellants used, thermally shock resistant, of low density, strong at very high temperatures, and has other characteristics such as high emissivity and good thermal conductivity.

A survey of the materials available has led to the choice of a few metal carbides which are reported to be the most refractory of materials. The carbides are characteristically hard and erosion resistant materials, they are stable at elevated temperature, and

they have a good measure of high temperature strength in combination with a reasonable thermal conductivity and emissivity. However, they are not low density materials, and at temperatures approaching their melting point weaken as other materials do. The only material which has mechanical strength at temperatures over 6000°F is graphite. To overcome the weaknesses of carbides a combination with graphite is ideal, for with well bonded surface coatings on graphite a system should be available which can have the high temperature strength of graphite and a low overall density. The chemical compatibility of the two materials is also ideal.

The pyrolytic deposition process was selected because it is the only technique which could produce carbides as coatings with optimum characteristics such as high density, homogeneity and purity. The process which produces materials by a gas phase reaction leads to the development of coatings which penetrate all surface irregularities of a substrate material. The mechanical adhesion of a pyrolytic coating to its substrate can be excellent and at the high process temperatures used chemical bonding can also play a role.

The need for highly refractory and erosion resistant materials for uncooled rocket nozzles where advanced solid propellants are used led to the investigation of pyrolytic carbides. Carbides produced by other techniques such as by plasma spraying and by powder metallurgy are also being prepared by a number of organizations and being evaluated for this application.

THE PYROLYTIC DEPOSITION PROCESS

The pyrolytic deposition process consists essentially of decomposing a volatile compound or a mixture of volatile compounds containing the desired constituents upon a heated surface. The process is carried out at elevated temperature, normally under reduced pressure and where a reducing gas, such as hydrogen, is used the process may also be carried out at or near atmospheric pressure. The deposits are nucleated on a surface called a mandrel or a substrate. With time the nuclei normally grow into a well defined crystal structure which may have a high degree of lattice plane orientation depending on the process conditions used.

The process variables which play a role during deposition are temperature, pressure, gas flow rates and the concentration of reactant gases. These variables affect the rate of deposition, the uniformity of the deposits, the grain size, and crystallite orientation as well as the composition of the material produced.

The pyrolytic process was first investigated by van Arkel[1, 2] for the development of zirconium, titanium and tantalum carbides. He used gaseous mixtures of the respective halides of the metals with carbon monoxide and hydrogen. Moers[3] investigated the carbide formation with gaseous mixtures of metal halide and a hydrocarbon such as toluene and hydrogen. Cambell and co-worker[4] has also studied the deposition of carbides by a similar technique. The reaction for the deposition of carbides is presented by the following general equation:

Metal Halide + Hydrocarbon + Hydrogen
Metal Carbide + Gaseous Products

Other processes are also used for the formation of carbide coatings. For example, metals are carburized with mixtures of hydrogen and a hydrocarbon and a carbide layer can be formed on graphite by the deposition of a metal which is simultaneously carburized by the diffusion of carbon from the substrate. There are other processes which are of lesser interest, such as the deposition of a carbide by the thermal decomposition of a volatile compound containing both a metal and carbon.

During the course of the present investigation, the direct deposition process was investigated because of the process control possible and the high deposition rates obtainable by the technique. The process using a three-gas mixture of a metal halide, a hydrocarbon and hydrogen was investigated. In some systems it is difficult to avoid the simultaneous deposition of a pure metal phase and for this reason with the fact that a three-component system should be more difficult to control than one which consists of only two components, a simplified process employing mixtures of a metal halide and a hydrocarbon was investigated. The investigation, limited in scope, was further simplified by use of only metal chlorides and methane. The deposition reaction may be written as follows:

$$MeCl_x + CH_4 \rightarrow MeC + HCl + \text{--------}$$

The deposition of a pure carbide depends on the relative decomposition rates of the gaseous compounds and possibly on a diffusion controlled mechanism. It was not part of the investigation to study the mechanism of deposition but only to develop a practical system for the deposition of carbides.

THE CARBIDES INVESTIGATED

The carbides which were investigated were selected because of their high reported melting points.[5] The following table lists the most refractory carbides and a few of their properties. It must be realized that these melting points were determined some time ago. The true melting points may deviate from these values by as much as a few hundred degrees; however, these carbides are likely to remain among the most refractory of materials.

Carbide	MP°C	MP°F	Structure	Lattice Const.	Density
4 TaC + HfC	3905	7125	F.C.C.	4.430	-
4 TaC + ZrC	3894	7105	F.C.C.	4.508	-
HfC	3890	7030	F.C.C.	4.64	12.7
TaC	3880	7020	F.C.C.	4.455	14.5
NbC	3500	6330	F.C.C.	4.46	7.8
Ta_2C	3400	6150	Hex	3.09-4.93	15.2
TiC	3250	5880	F.C.C.	4.32	4.9
ZrC	3175	5750	F.C.C.	4.685	6.4

The carbides which were investigated are HfC, TaC and NbC. The first two carbides are the most refractory single carbides but also the heaviest with densities of 12.7 and 14.5 gms/cc respectively. The least refractory, NbC, also has a lower density of 7.8 gms/cc. All the carbides have characteristic high hardness which range on

the knoop microhardness scale from 1800 to 2400 with a 100 gram load. The hardness of a material is related to its mechanical erosion resistance and on this basis these materials should be highly erosion resistant.

The selection of these carbides as surface coatings on rocket nozzles for use with solid propellants is justifiable on a refractory and hardness basis. With respect to their vapor pressure at very high temperatures, it may be stated that the materials will melt before they sublime and that from the meager vapor pressure data available that TaC is more stable than NbC.

EQUIPMENT DEVELOPMENT

The equipment required for the investigation which included the development of the process, the fabrication of samples for property evaluation, the preparation of carbide coated test nozzle inserts and the development of carbide coated full scale Polaris nozzles may be divided into two types. One was the design and construction of a system used solely for process development. This system made use of a resistively heated wire which was also the substrate. The second system was the conversion of standard graphite resistance heated units which provided a hot zone into which could be introduced mandrels or components to be coated.

The basic process equipment consists of a chamber which contains a heating element, an electrical power supply, a vacuum pumping system with pressure metering gauges and solid particle and/or vapor trapping systems, and a source gases metering system.

Two system components required development for accurate control of the process. One was a halide metering system. The metering of halides which are solid at room temperature has been accomplished in the past by control of the vapor pressure of halides and by use of a carrying gas. For accurate control of the flow of halides, which is important where two source gases are used, a positive metering system was required. The other component was an injector with which to transfer the gaseous halides to the not zone or deposition area of a furnace without condensation.

The first phase of the program was an investigation of the process for the deposition of pyrolytic silicon carbide which would be used as a model for the processing of other carbides. The source material, silicon chloride, is a liquid at room temperature; and it was predicted that this compound would be easier to use and that process information would be easily obtained.

The metering system developed for the control of the flow of $SiCl_4$ is shown schematically in figure 1. The system is a glass unit which consists of a graduated glass tube container which contains the $SiCl_4$ charge. Argon gas is supplied to maintain the space above the liquid at atmospheric or at a desired pressure level. A fritted glass filter was required to prevent clogging of the capillary with small amounts of solids found in the halide. The capillary restricts the flow of liquid halide which is controlled by means of a pressure differential across the liquid charge. In practice it was found that a variable capillary such as a small bore stopcock was desirable for better control of the flow. The evaporator is a heated section of line which vaporizes the halide prior to its injection in the reaction chamber.

Other systems were also investigated such as the one shown in figure 2. This unit is simply an evaporation system where the evaporation rate is controlled by the temperature of the liquid. The rate of evaporation is measured by means of a calibrated column.

LIQUID HALIDE METERING SYSTEM

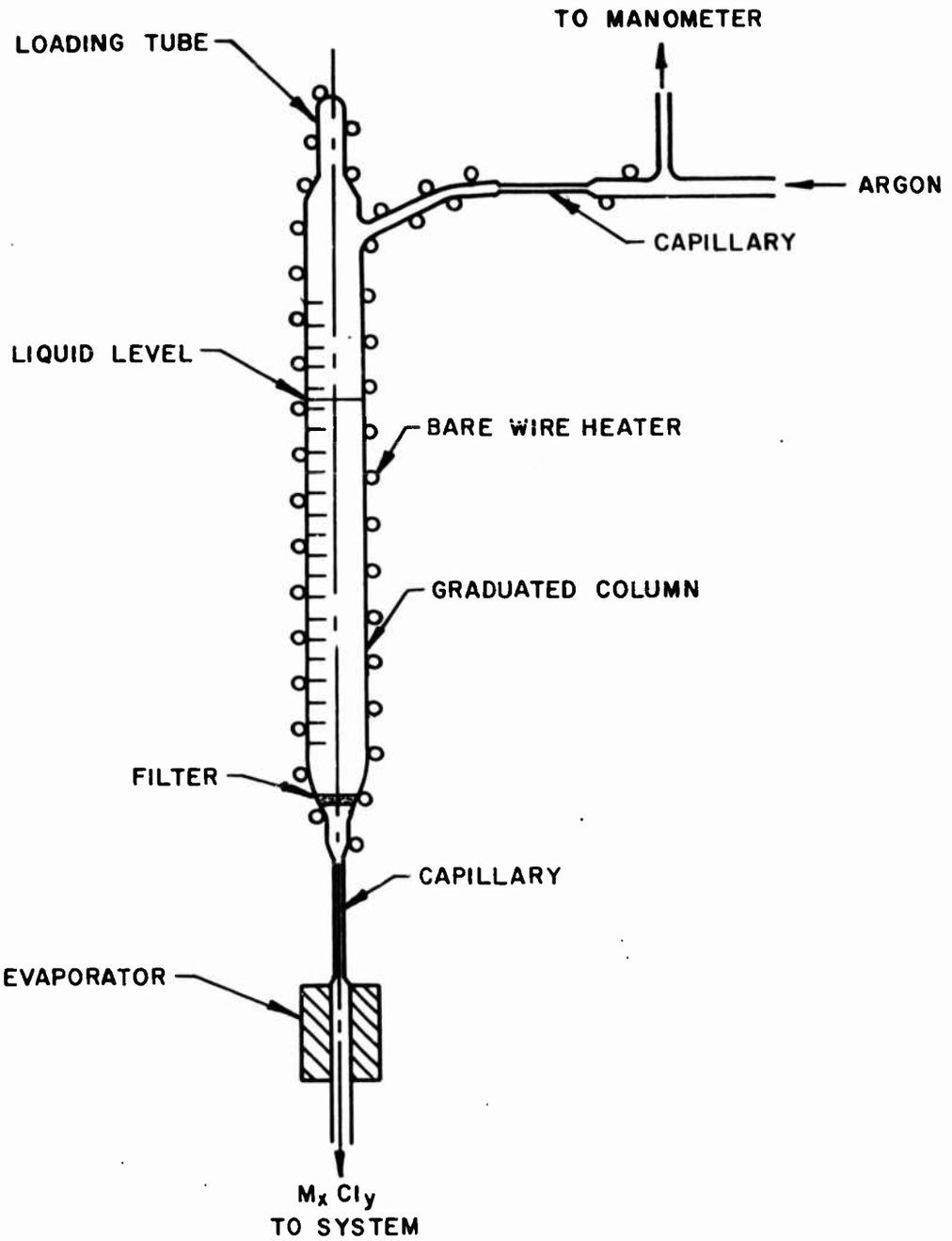


FIGURE 1

LIQUID HALIDE METERING SYSTEM

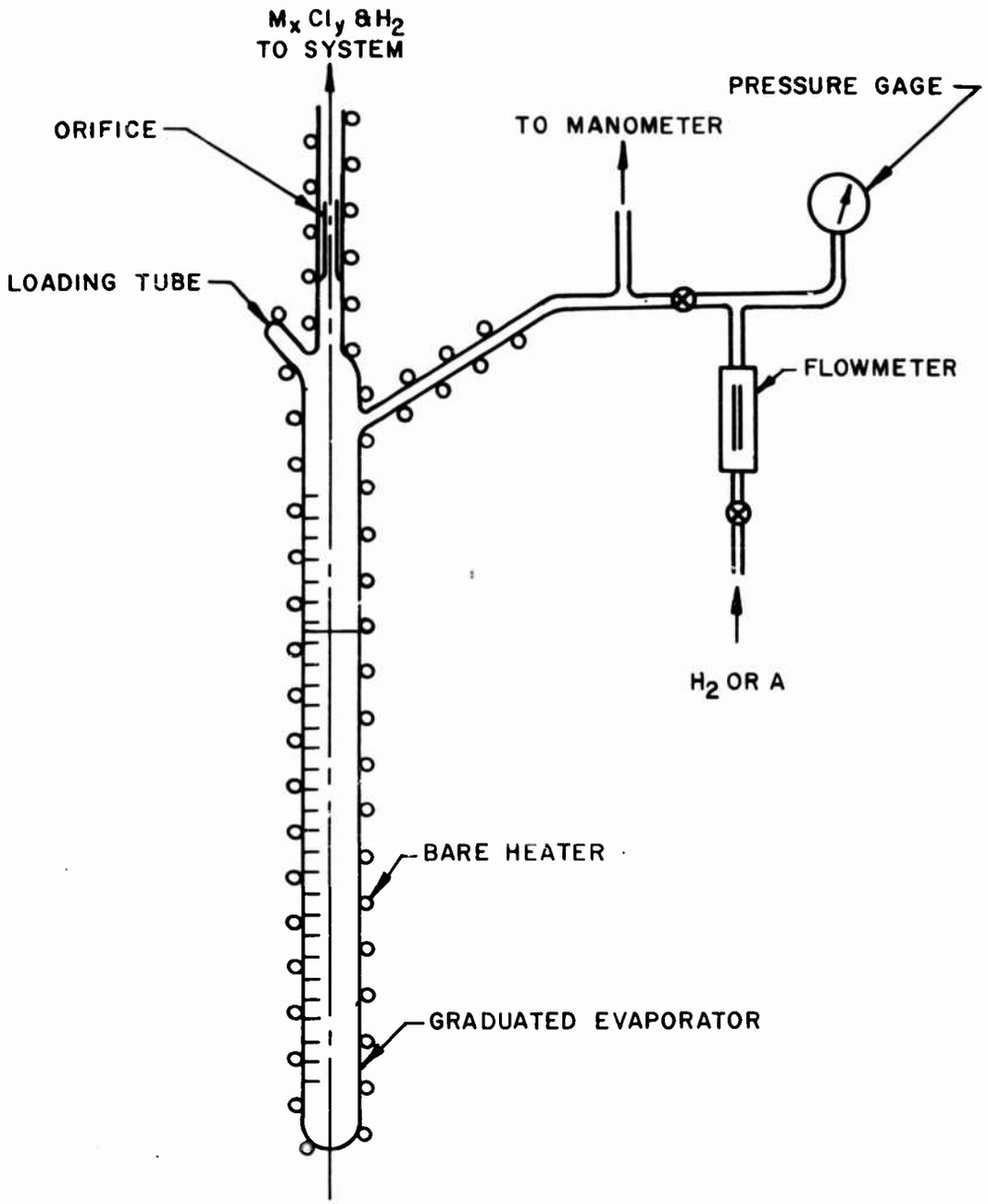


FIGURE 2

The former system was found to be the most accurate metering system. The flow of silicon halide could be maintained at a constant value throughout an experimental run without difficulty. For the metering of liquid halides this system is satisfactory. The metering of halides which are solid at room temperature presents a greater challenge. The evaporation technique was initially used but found inadequate. The development of metering systems progressed through the evaluation of a number of units to the point where two systems were acceptable.

One halide metering system investigated was the solid halide metering system which is shown in figure 3. The control of the flow of halide was obtained by vaporizing a column of powdered or solid halide at a desired rate. The feed rate of the material to an evaporator controls the rate of evaporation of the halide. The motorized screw provided travel of the halide column to an evaporator section. This section is merely a restricted zone maintained at a temperature near or above the boiling point of the halide. This system performed satisfactorily after the evaporation rate and feed rate of the halide were equated. During start up a variable flow rate was obtained which was reflected in most cases in the structure of the material produced.

The metering system shown in figure 4 provided a constant flow rate from the start of operation. The flow of halide in this case is determined by the feed rate of powdered halide to an evaporator.

SOLID HALIDE METERING SYSTEM

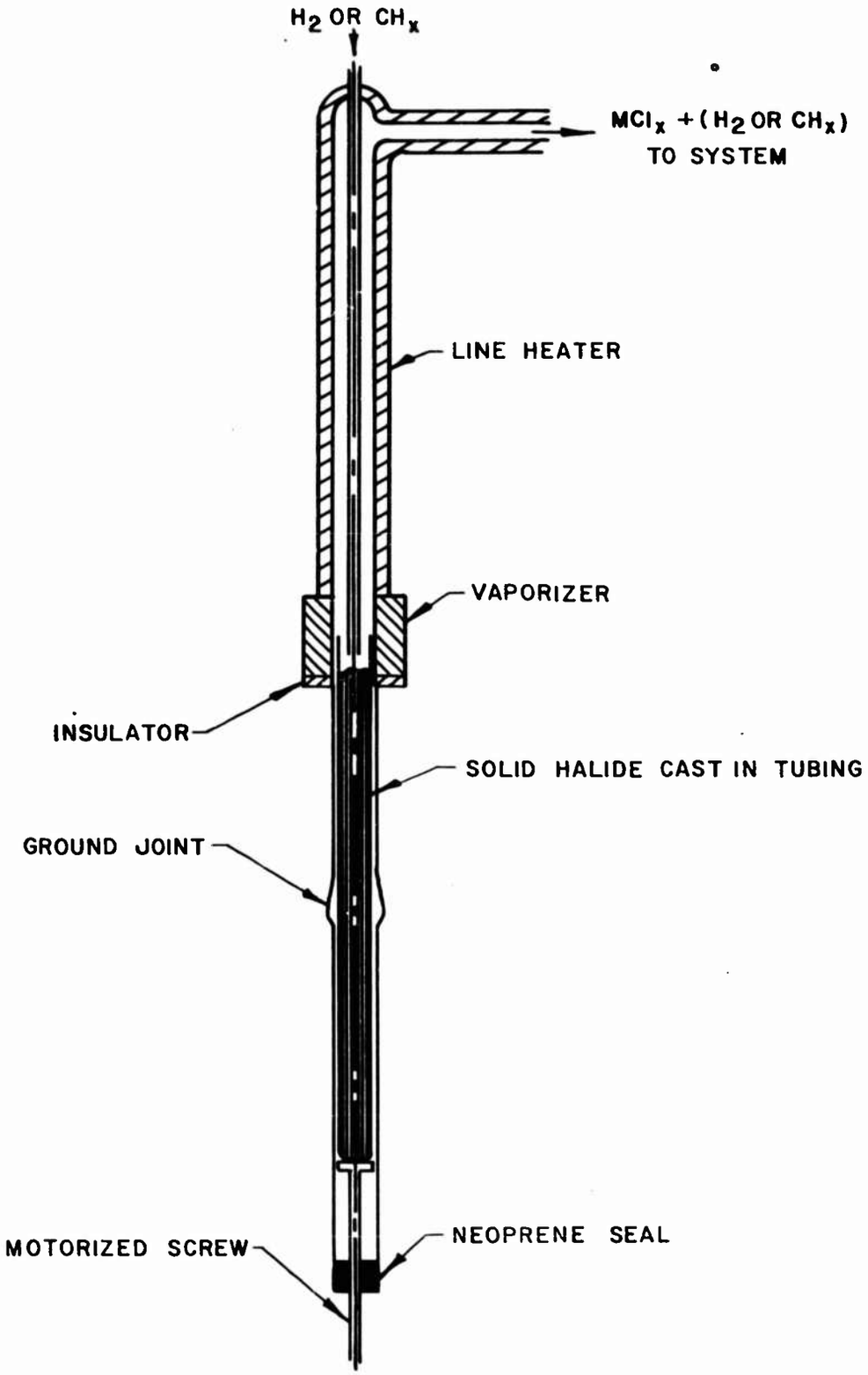


FIGURE 3

HALIDE POWDER METERING SYSTEM

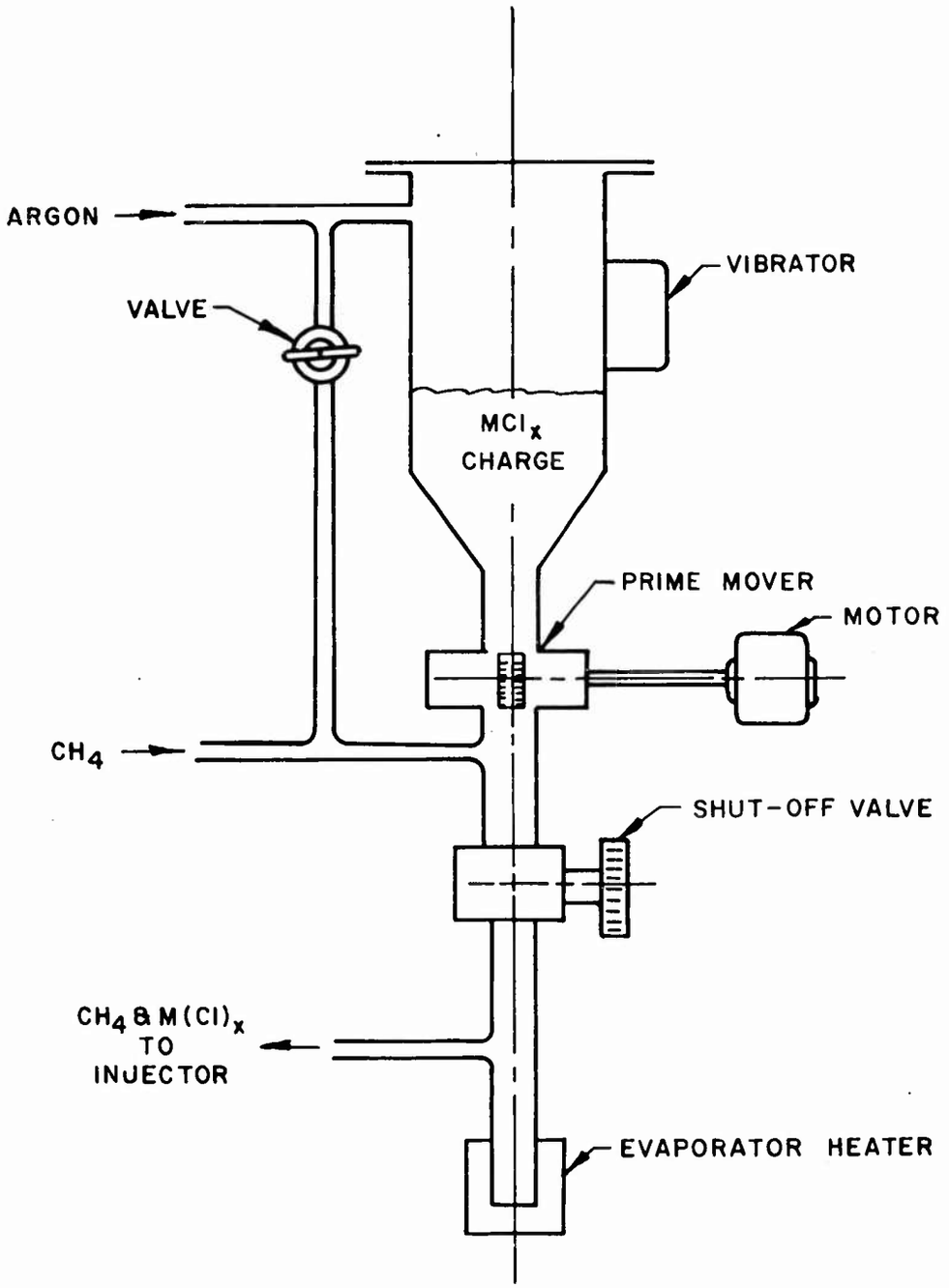


FIGURE 4

When the evaporator, which may be a section of feed line, is maintained above the boiling point of the halide the evaporation rate is equal only to the material feed rate. The halides, specifically $TaCl_5$, $HfCl_4$ and $NlCl_5$, are obtainable as fine powders. Before use the material must be sifted to remove all agglomerated lumps of material to ensure their proper metering. The prime mover is a paddle wheel arrangement which merely transfers the powdered halide from a container to the evaporator. The secondary gas, methane in this case, is introduced with the powder stream so that it prevents the back diffusion of halide vapors to the powder feed mechanism. Argon is used for the same purpose and also to eliminate pressure differentials in the system. Two notes of caution are required for the proper use of this system: One, the vibration required for the proper flow of halide powders must not be so evident that it causes compaction of the powders; and two, the halide powders used must be pure and uncontaminated by even traces of water which causes the powders to agglomerate. Such a system has been operated successfully and will produce the desired halide flow rates.

A third system which was also proven for metering halides is shown in figure 5. The unit is simply a flowmeter which is maintained at a sufficiently high temperature to prevent the condensation of metal halides. To maintain the flow at a constant value the vapor pressure is kept constant by controlling the temperature of the evaporator. The flow rate is also controlled by means of a hot

HOT FLOWMETER METERING SYSTEM

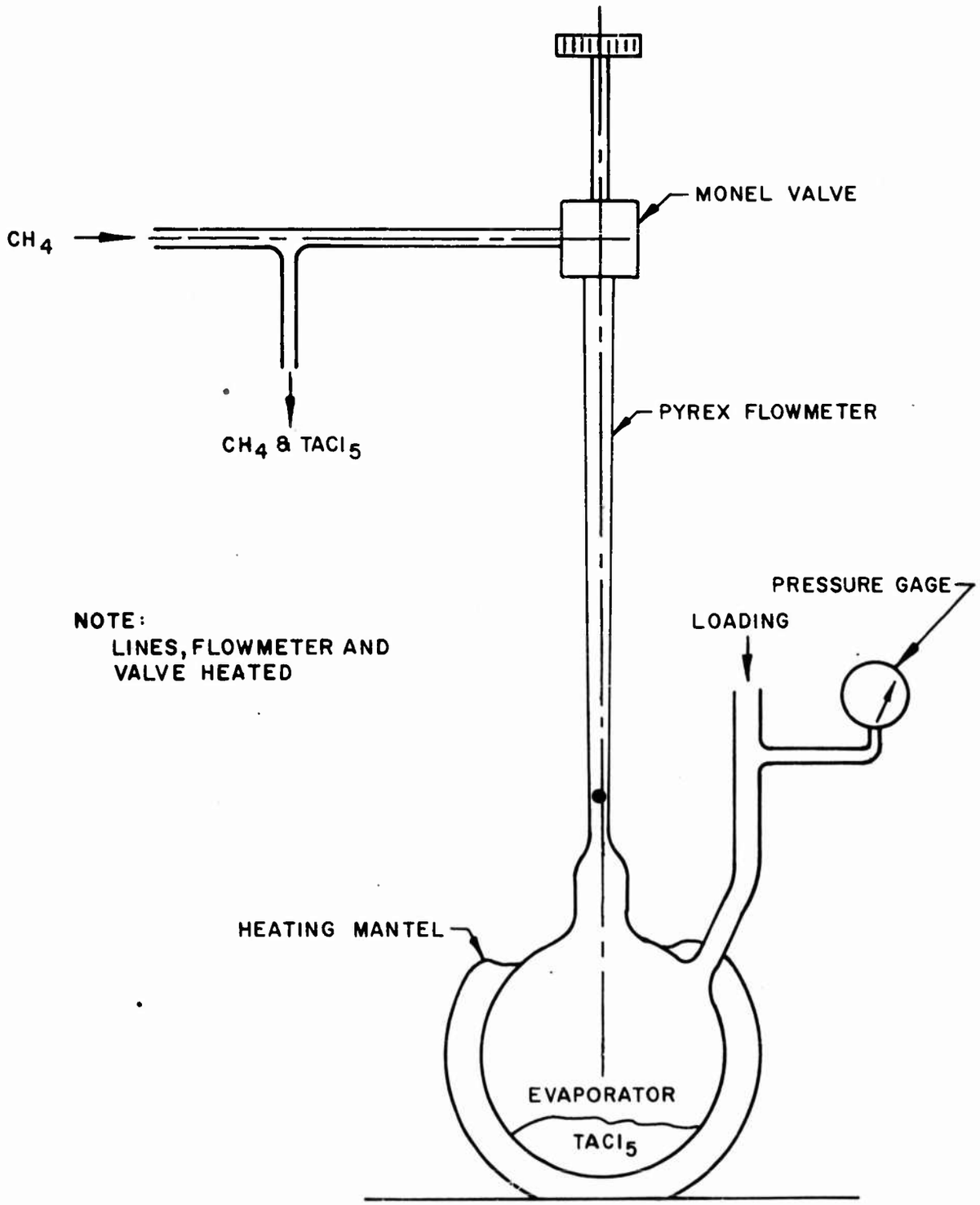


FIGURE 5

valve. It may be realized that the flow rate of the halide is dependent not only on the temperature of the halide charge but also on the system pressure. The unit developed permits the control of both dependent variables and controls the flow in a reproducible and adjustable manner. This system was used successfully for the metering of $TaCl_5$ and $NbCl_5$, and could be used for metering the other metal halides.

The metered halides which may be premixed with other source gases must be introduced into the deposition area of a system. The system used to perform this task is called an injection system or simply an injector. The injector is basically a water cooled tube. To handle condensable metal halides the injector must serve a second function; that is, the introduction of those vapors through metal flanges and seals without their being condensed at any joint in the system.

Initially, gas and oil cooled injectors were investigated. The gas cooled systems did not perform satisfactorily because of their relatively low heat capacities. Oil cooled injectors were also unsatisfactory mainly because of the instability of oils when used at temperatures in the $300^{o}C$ to $400^{o}C$ range. A satisfactory injector was developed which incorporates a heated central injector tube which is surrounded by a water cooling jacket. The central source gas tube is maintained at temperatures above the condensation joint of metal halides by means of a resistance wire embedded in a

ceramic tube. This is the only modification of a standard water cooled injector which was required.

The process investigation equipment which was utilized during the first phase of the program is shown in figure 6. The apparatus consists of a Vycor reaction chamber which contains a resistance heated wire of Mo or W. The wire is also used as the substrate onto which carbide deposits were obtained. The wire is held in position by means of a water cooled electrode. A 200 V power supply, powerstat controlled, was used to obtain wire temperatures up to the melting points of the wires used. Temperatures were measured optically through a side port on the reaction tubes. The side port, not shown, was added before the equipment was placed in operation. The control panel at the right of the photograph contains the powerstats and indicating pyrometer for control of line and component temperatures. The gas control panel, which contains standard flowmeters, is not shown in the photograph. The metering system shown is a solid halide controlled feed unit which introduces the vertical column of halide by means of a screw mechanism to an evaporator section. The source gas line as well as the reaction chamber are wound with resistance wire to prevent the condensation of halide. The pumping and trapping systems, which are standard, are positioned below the unit.

The above system produced a great number of experimental runs in a relatively short time and was useful for preliminary information on the formation of pyrolytic carbides and was also useful for

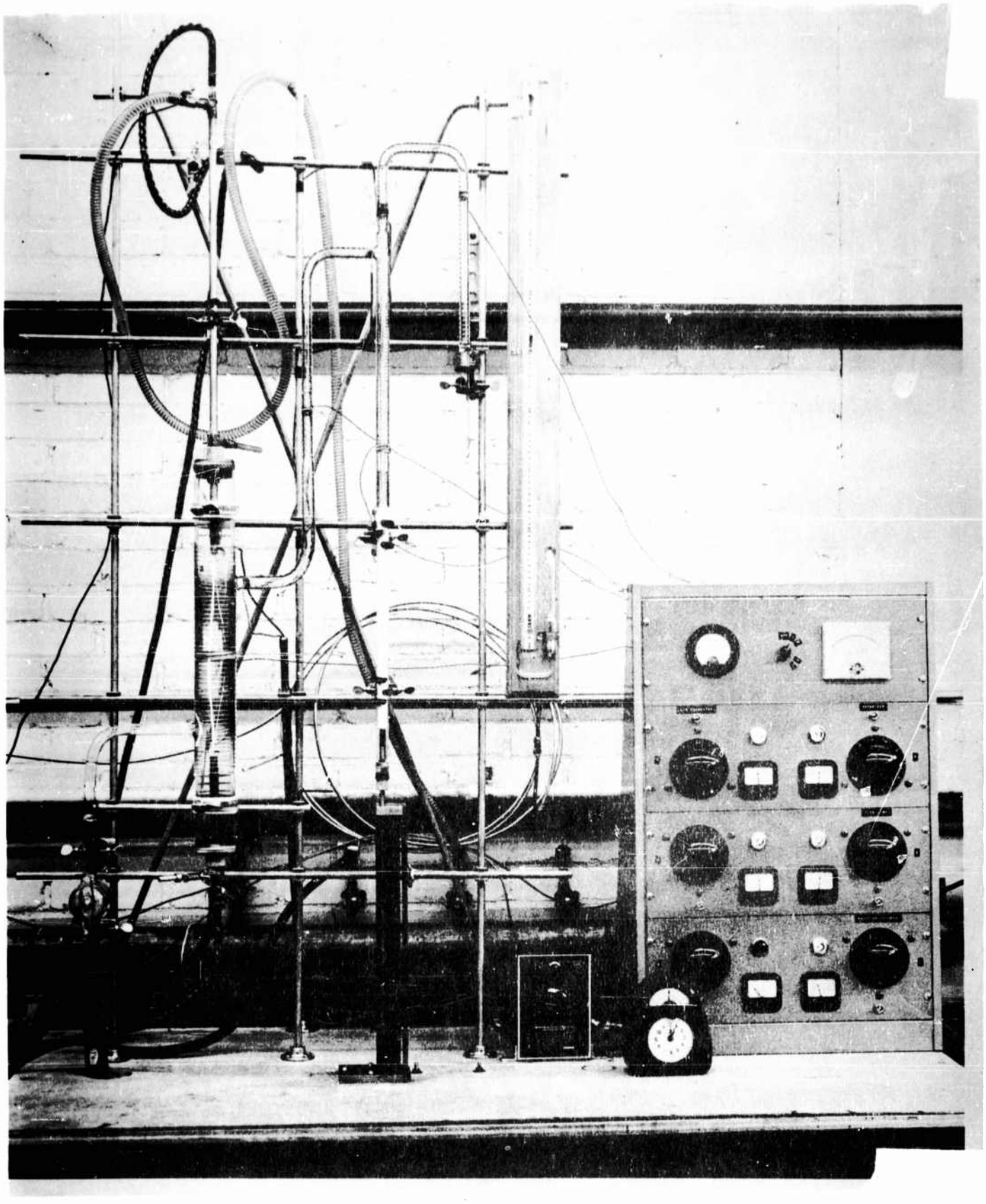


Figure 6 Hot Wire Apparatus

evaluating metering and other systems. The disadvantages of such a system are that accurate measurement of deposition temperatures is difficult to obtain and maintain, and only small amounts of materials can be produced at any one time.

The resistance furnaces, which permitted the development of carbides in large sample sizes and which were also used for carbide coating of test nozzle inserts, is shown in figure 7. The units are double walled water cooled chambers which contain a 3" I.D. x 8" long and a 4" I.D. x 8" long graphite resistance element. The elements which are surrounded by insulation are connected to horizontal water cooled electrodes. The power supplied to these units is a 50 KVA unit. The vacuum and filter systems are positioned in the rear of the unit. The left unit was adapted with the hot flowmeter type metering system; and, as can be noticed, the metal halide container, the flowmeter, the lines leading to the injector and the methane gas line are heated with wire resistance units. The injector is inserted in the top flange and introduces the source gases into the system. By-product gases are exhausted through the bottom flange and cold trap seen in the photograph. The modification also includes the electrical panel positioned on top of the units.

The right hand unit was used initially for the SiC investigation. The metering system for $SiCl_4$, which was incorporated in the system, was described earlier. At the time this photograph was taken the furnace was being modified by the installation of a powder feed metal halide metering system.

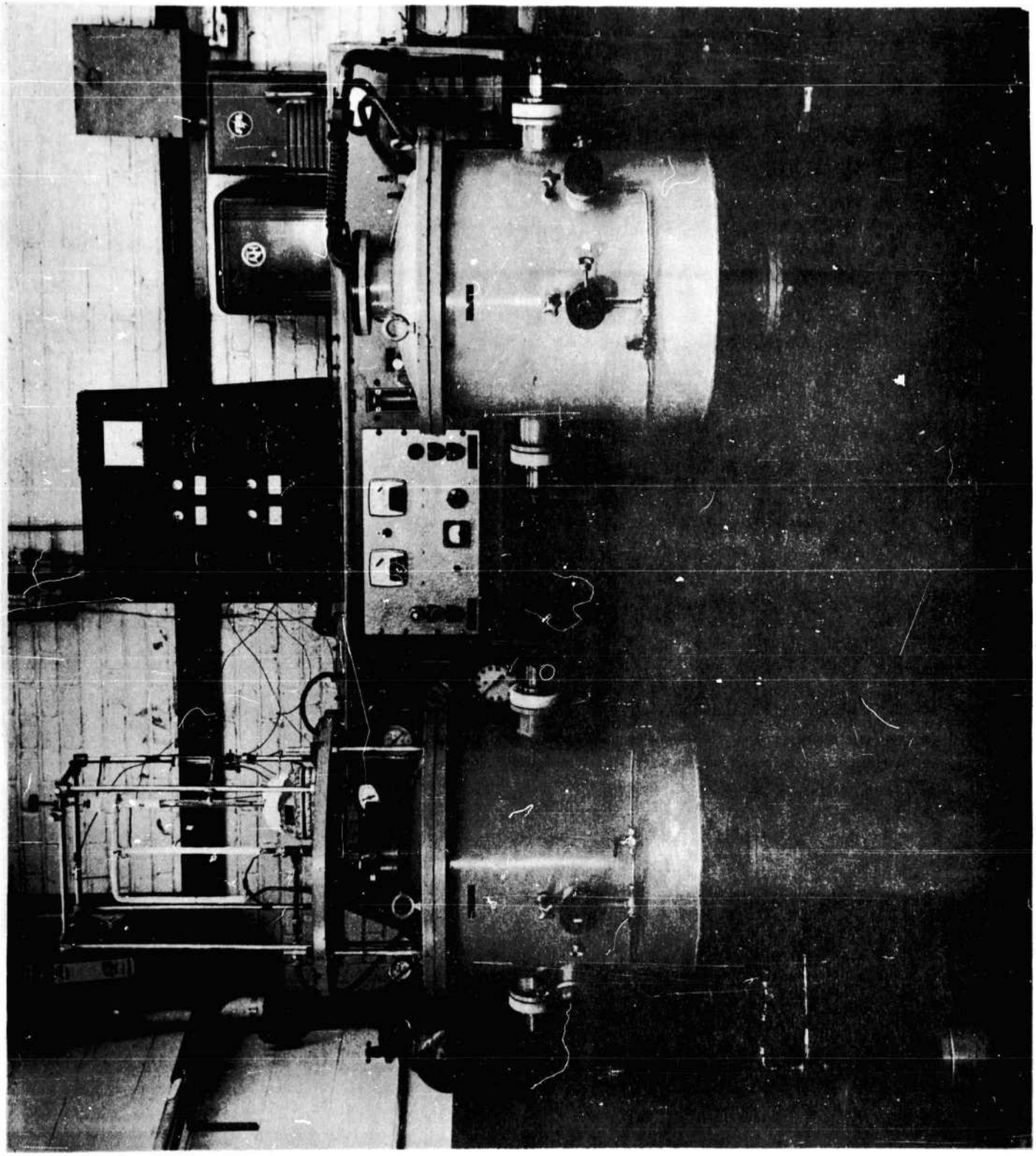


Figure 7 Laboratory Resistance Furnaces

A larger resistance unit which contained an 8" I.D. graphite element was modified for the development of carbide coated full scale Polaris throat nozzle sections. This system shown in figure 8 made use of the halide powder metering system previously described. The metering system is seen positioned on the top flange of the furnace. The uppermost component is the powdered halide hopper. The powder feed mechanism and motor are attached to the top platform which is removable for access to the evaporator situated below it. The evaporator is simply an enlarged piece of tubing which is water cooled at the top and resistance wire wound over its lower section. The evaporator tube is connected directly to the injector. All of the electrical controls for the metering and injector systems are mounted in the panel seen in the left of the photograph. The other furnace modifications made included the installation of an 11" x 18" long graphite resistance element along with new and improved side electrodes. The element was surrounded with insulation next to the water cooled chamber walls and at both its ends. The by-product gases were exhausted through the bottom flange and through a separate exhaust line, filter and vacuum pump system. The main control panel on the front of the unit includes the secondary gas metering system (methane and argon), the pressure indicating system as well as the electrical power control panel. The power supply for the system is a 75 KVA unit which permits operation to temperatures in excess of 2200°C.

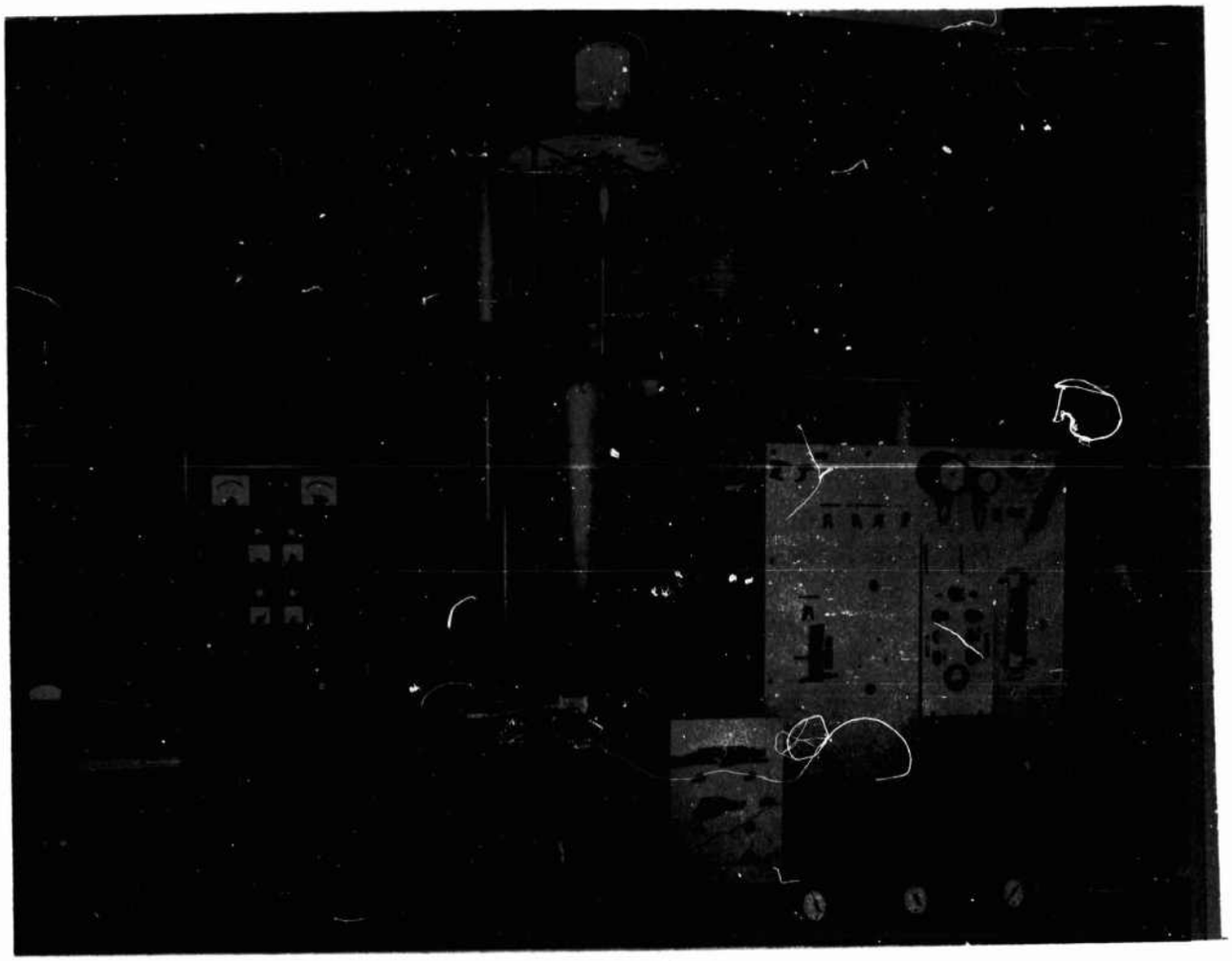


Figure 8 Equipment for Processing of Full Scale Nozzles

During the course of this program a number of systems and components have been investigated and employed. A general schematic of the process equipment used for the deposition of carbides is shown in figure 9.

SCHEMATIC OF PYROLYTIC DEPOSITION EQUIPMENT

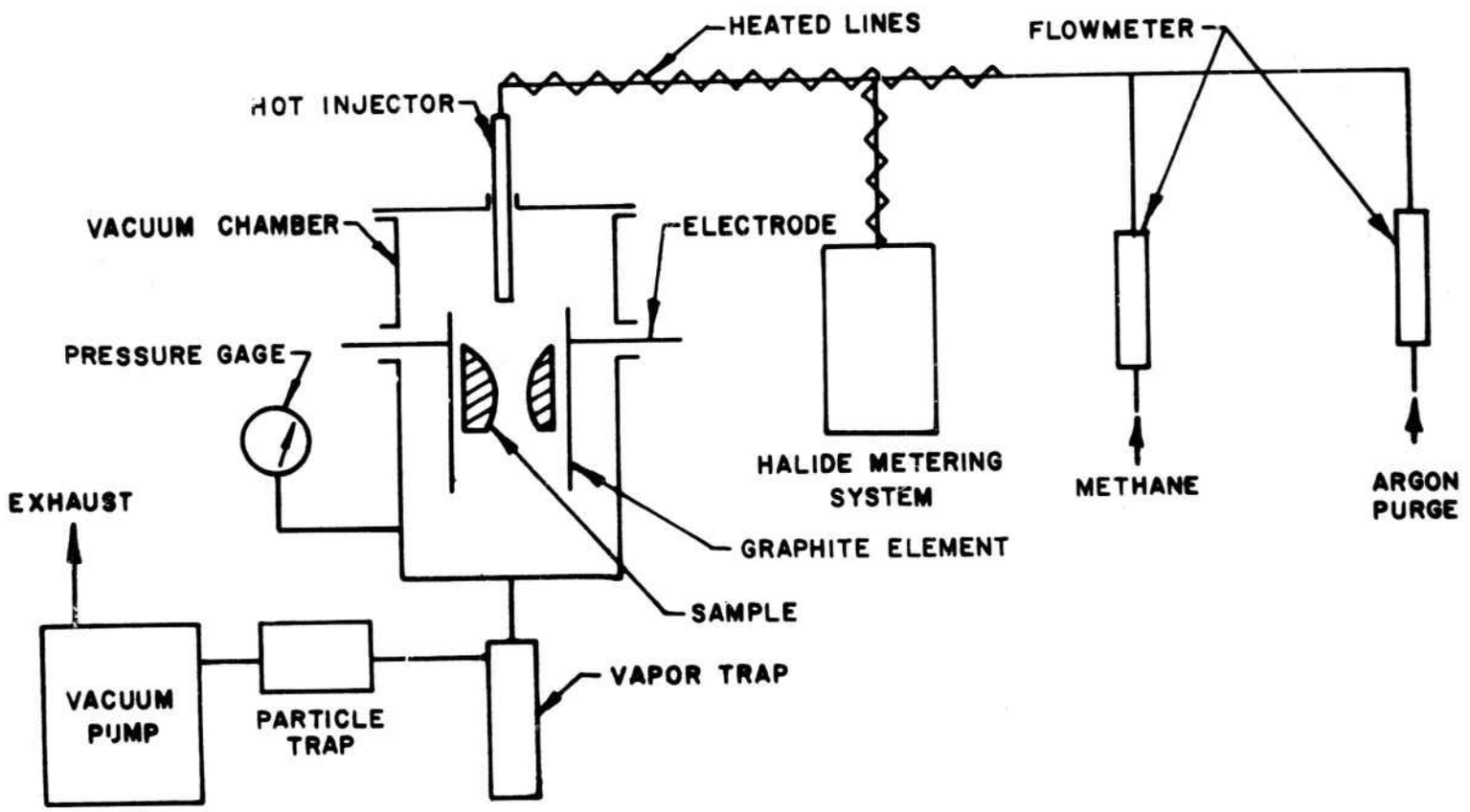


FIGURE 9

PYROLYTIC SILICON CARBIDE

The deposition of silicon carbide was the first investigation undertaken on this program. The investigation was made primarily for the purpose of developing a pyrolytic deposition process for the carbides. The source gas chosen for silicon was $SiCl_4$, a liquid at room temperature which is relatively inexpensive and more easily metered than solid halides.

The use of hydrogen for the deposition of carbides lowers deposition temperatures but in some cases makes it difficult to avoid the simultaneous deposition of pure metal. For this reason hydrogen was not employed for the investigation of silicon carbide deposition. The source materials used and the general process reaction are presented in the following equation:

$$SiCl_4 + CH_4 \longrightarrow SiC + 4HCl$$

The mixed source gases were introduced or injected into the reaction zone of a resistance furnace maintained under reduced pressure and at elevated temperature. The substrate components coated were graphite and molybdenum in the form of tubes and rectangular coupons. The tubes were approximately 2" I.D. x 8" long and the coupons 1" wide x 6" long.

A total of 48 experimental runs were made during the investigation to determine the influence of process variables on the deposition rate, the extent of deposition, and the crystal structure

of the material produced. Simultaneously, the equipment used was modified and improved; and metering systems as well as injectors were evaluated.

The process variables investigated were the following:

1. Temperature;
2. Pressure;
3. $SiCl_4/CH_4$ ratio;
4. Source gases flow rate.

The process variables range investigated was:

1. Temperature - 1300°C to 1900°C
2. Pressure - 3 to 600 mm
3. $SiCl_4/CH_4$ - 1/2 to 20/1
4. $SiCl_4 + CH_4$ - 0.2 to 2.3 gms/min.

The influence of temperature was found to be twofold. At temperature lower than 1500°C the decomposition rates are low and the deposition rates correspondingly low. At the higher temperatures in the region of 1900°C the deposition rate is also low and appears to be due to the relatively high vapor pressure of SiC at these temperatures. As the temperature increases the grain size of the deposit also increases. The effect of pressure variation was found to be related to the temperature. The lower the pressure the higher the decomposition rate of the $SiCl_4$ but the higher the vaporization rate of the SiC. Optimum values for temperature and pressure exist which from a deposition rate standpoint are 1500°C to 1700°C at 400 mm.

In terms of structure the higher the temperature the larger the grain size; but other variables such as the gas flow velocity, pressure, and the $SiCl_4/CH_4$ ratio appeared to play a role.

The $SiCl_4/CH_4$ ratio was found to be important in determining the structure of the material produced. A two phase material containing both SiC and free carbon was normally found when the $SiCl_4/CH_4$ ratio used was below 10.6 on a weight basis. The effect of total gas flow rate was primarily in the distribution of coating thickness in the direction of the gas flow. As may be expected the lower the gas velocity the more localized the deposits.

The efficiency of the process based on 100% utilization of methane was found to lie between 1 and 54%. However, the higher values obtained were not realistic because the structures contained both SiC and carbon. It was estimated that the highest efficiency obtained based only on SiC formed was closer to 20%.

A cross section of a dense SiC deposit is shown in Figure 10. The grain structures is not shown because of the resistance of this material to normal chemical attack. The microhardness of vapor deposited silicon carbide was found to be approximately 2500 on the knoop scale with a 100 gram load. The hardness of this material is, therefore, comparable to that of commercial silicon carbide.

The material produced was identified by X-ray diffraction as β silicon carbide with a lattice parameter of 4.34, a value

Silicon Carbide

Unpolarized

100 X

Unetched

Figure 10

which correlates with an accepted value of 4.349Å for this material. It was also determined from line intensity variations as related to hkl reflections that pyrolytic silicon carbide has little or no crystal anisotropy.

From the results obtained on the deposition of silicon carbide it became apparent that the processing range for producing this material might be different from the processing range for producing the more refractory carbides. The deposition temperatures for SiC are above the melting point of pure silicon, whereas the processing temperature for TaC and NbC would of necessity be lower than the melting points of the respective metal constituents. This means that the deposition of pure silicon was avoided while the simultaneous deposition of Ta and Nb with their carbides would have to be eliminated. In addition, the vapor pressure of silicon carbide requires a compromise set of operating conditions for optimum deposition rates. The value of the investigation was in the equipment development phase and in a demonstration of the feasibility of producing carbides with a two-component source gas system.

PRELIMINARY REFRACTORY CARBIDE INVESTIGATION

The first phase of the investigation for the deposition of the refractory carbides, hafnium carbide, tantalum carbide and niobium carbide, was performed with the hot wire apparatus previously described. The molybdenum and tungsten wires used as substrates were heated electrically to deposition temperatures. The size wires used were limited to diameters in the range from .005 to 0.010 inch and in length from 6 to 10 inches.

Wire temperatures were measured with an optical pyrometer and corrected to actual temperatures, from a pre-calibration curve obtained by measuring the melting points of metals such as titanium, platinum, zirconium and molybdenum.

The advantages of the hot wire technique lie principally in the fast cycling obtained; heat up and cool down times are extremely rapid. The disadvantages were that the deposition temperature which varied during deposition was difficult to maintain at a constant value and only small amounts of material could be produced.

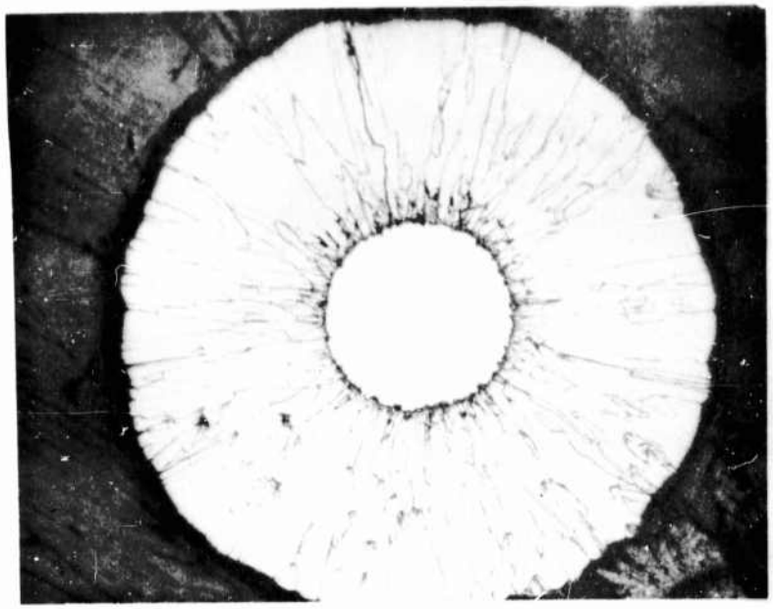
The evaluation of the materials produced was obtained by metallographic examination and with microhardness surveys. Metallography revealed the grain structure, grain size and the number of phases present in the deposits. Microhardness measurements were used for determining the presence of the hard carbide phases. Spectrographic analysis of carbide deposits were obtained but the results were inconclusive.

A first series of 33 experimental runs was made on the hot wire apparatus for the investigation of hafnium carbide deposition. The source gases used and the general deposition reaction are given in the following equation:

$$HfCl_4 + CH \longrightarrow HfC + HCl$$

Hafnium tetrachloride is a solid at room temperature which was metered during this series of experiments with the solid halide controlled feed mechanism previously described. The deposition temperatures investigated were in the range from 1500°C to 2400°C. The lower limit for HfC deposition was found to be 1500°C where only low deposition rates were obtained. Appreciable deposition rates were obtained only at a temperature of 1650°C and higher. At temperatures below 1700°C the deposited structures consisted of HfC with, in most cases, isolated pyrolytic graphite or carbon crystals.

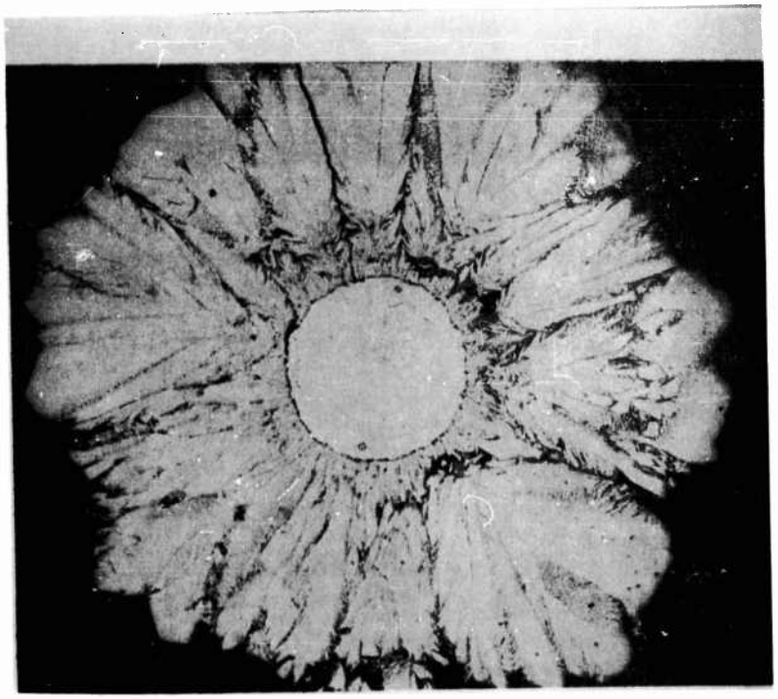
Increasing the deposition temperature also increased the grain size of the deposits. Figure 11 shows a HfC deposit on tungsten wire obtained at 1700°C with a $HfCl_4/CH_4$ mole ratio of one, and figure 12 shows a coarser grained material produced at 2100°C with the same source gas ratio. The deposition rate of this sample produced at 1700°C was 40 mils/hr. while that of the 2100°C sample was 85 mils/hour. In general, it was found that the deposition rate increased with increasing temperature but at the expense of an increasing grain size.



Hafnium Carbide 100 X

Unpolarized Etched

Figure 11



Hafnium Carbide 100 X

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Figure 12

The effects of the $HfCl_4/CH_4$ ratio and the reaction pressure were also briefly investigated. The conclusions drawn were that higher halide to methane ratios are required at higher temperatures in the range of 2200°C to 2400°C in order to avoid the simultaneous deposition of carbon. Increasing the system pressure resulted in the production of finer grained deposits.

Microhardness surveys were obtained for all phases present in the microstructures. The Knoop microhardness number of the identifiable HfC phase was found to be in the range of 2100 to 2300. In comparison the microhardness of HfC is reported to be 2200 and that of molybdenum wire substrates found to be in the region of 400 to 500.

A second series of thirty-eight experimental runs was made for the investigation of tantalum carbide deposition. The source gases used and the general deposition reaction are given in the following equation:

$$2TaCl_5 + 2CH_4 \longrightarrow 2TaC + 8HCl + Cl_2$$

Tantalum pentachloride which is a solid at room temperature was metered by the same technique used for metering hafnium tetrachloride. The process variables investigated were the deposition temperature and the $TaCl_5/CH_4$ ratio. The reaction pressure was maintained in the region below 1 mm of mercury for all experimental runs. The lower limit for tantalum carbide deposition was found to be 1500°C but appreciable rates were

obtained only at 1700°C and at higher temperatures. The temperatures required for the deposition of tantalum carbide are, therefore, in the same range as the temperatures required for the processing of hafnium carbide.

The $TaCl_5/CH_4$ mole ratios were varied from 1/1 to 4/1 and it was found that ratios greater than 1/1 were required to produce single phase materials. Figure 13 shows a tantalum carbide coating on a tungsten wire substrate produced at 1700°C. Due to a metal halide to methane mole ratio which was initially less than 2/1 a carbide with a secondary carbon phase was produced next to the wire. The outer coating is a typical golden colored tantalum carbide layer.

The deposition rates obtained were mostly in the range of 40 to 60 mils per hour with the rates generally increasing with increasing deposition temperatures.

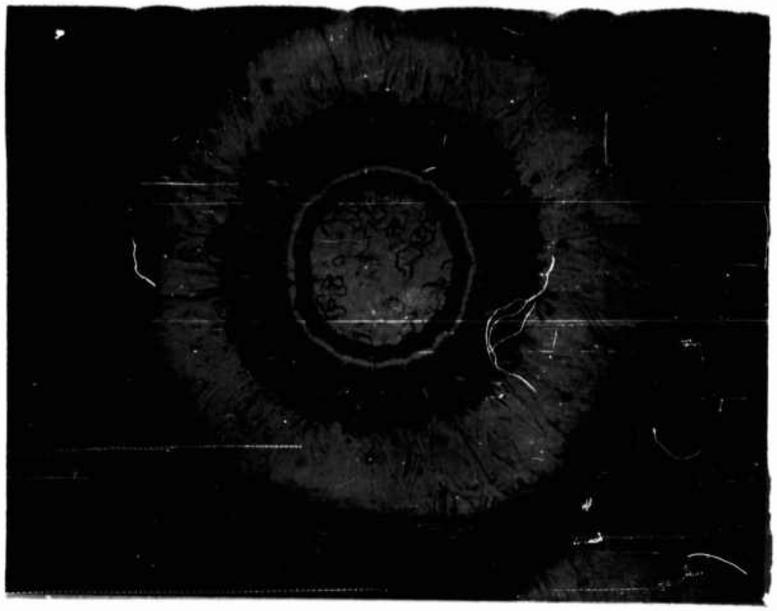
Microhardness surveys of materials identifiable as tantalum carbide revealed that the Knoop microhardness was in the range from 2200 to 2600. The microhardness of tantalum carbide is reported to be 1800, a value lower than the carbide produced pyrolytically. As will be shown later tantalum carbide with lower microhardnesses can be produced by this technique.

A third series of 26 experimental runs was made for the investigation of niobium carbide deposition. The source gases used and the general deposition reaction are given in the following equation: $2NbCl + 2CH_4 \longrightarrow 2NbC + 8HCl + 2Cl_2$

The niobium pentachloride, which is also a solid at room temperature, was metered by the same technique used for the other halides.

The deposition temperature range investigated was between 1700°C and 2100°C with system pressures from below 1 mm to 15 mm of mercury. Metal halide to methane mole ratios were varied from 1/4 to 1/1.

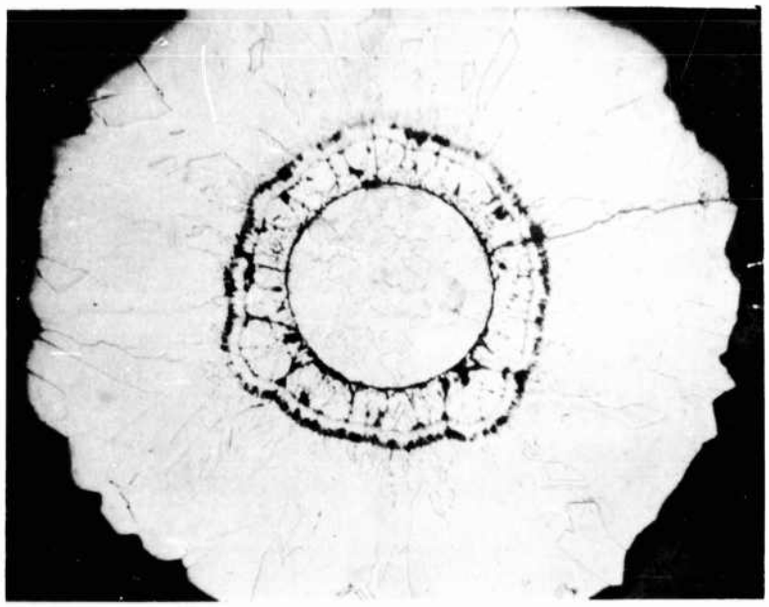
The results obtained were similar to the results obtained for the hafnium and tantalum carbides. This limited investigation revealed that a temperature of 1700°C is required for the deposition of niobium carbide. Within the pressure range investigated there was not any measurable difference in the deposition rate. The importance of an accurate halide metering system was well emphasized from the microstructures obtained. The halide metering system used did not provide a constant halide flow rate for some time after the start of operation, and as a result most of the coatings produced contained layers of different composition. Figure 14 shows a niobium carbide coating on a tungsten substrate produced at 1900°C, at less than 1 mm of mercury pressure and with a $NbCl_5/CH_4$ mole ratio of 1/1. The inner band contains carbide with some carbon interspersed in the structure while the outer band is a typical dense niobium carbide structure. The coating next to the wire substrate was produced in this case with a metal halide to methane ratio which was less than unity.



Tantalum Carbide — 100 X

Unpolarized — Etched

Figure 13



Niobium Carbide — 100 X

Unpolarized — Etched

Figure 14

The deposition rates of niobium carbide at 1900°C was found to be in the range of 80 to 100 mils per hour. At reduced temperatures the deposition rates were normally lower. The microhardness on the Knoop scale of a single phase niobium carbide was found to be in the range from 2300 to nearly 2900. The microhardness of commercial niobium carbide is reported to be from 2400 to 2470.

The combined results of the investigation performed using the hot wire technique are as follows:

1. The feasibility of producing single phase tantalum carbide, hafnium carbide and niobium carbide was established.
2. A two source gas system composed of a metal chloride and methane can produce single phase carbides by a simultaneous thermal decomposition process.
3. The lower temperature limit for the deposition of these carbides is 1500°C but appreciable deposition rates are obtained at 1700°C and higher temperatures.
4. The mole ratio of metal chloride to methane should be equal to or greater than one depending on the deposition temperature and possibly on the pressure of the reaction. Only small differences in ratio appear to be required for the deposition of the above named carbides.
5. The pressure of the reaction affects the grain size of the material produced in some cases. Increases in pressure tends to reduce the grain size but other factors such as source gas velocity may play a role.

6. High deposition rates were normally obtained which increase with increasing deposition temperatures. These rates were obtained on wires and may not be representative of the rates obtained on flat surfaces.
7. In order to produce single phase carbides pyrolytically an accurate halide metering system is required. Changes in the metal halide to methane ratio leads to the deposition of a secondary phase. Temperature variations do not appear to be as detrimental in this respect.

THE DEPOSITION OF REFRACTORY CARBIDES

The three refractory carbides, namely TaC, HfC and NbC were produced on a larger scale in high temperature resistance furnaces. The process equipment employed were the two laboratory units with hot zones of 3" and 4" diameter by 8" long. The equipment was used for four tasks: One, the development of halide metering systems and injection systems; two, the development of the process on a larger scale; three, the coating of flat plate mandrels normally 1" wide by 5" long for material evaluation; four, the preparation of carbide coated test rocket nozzle inserts.

The metal halides were metered with two different metering systems. Tantalum pentachloride was metered with the hot flowmeter system previously described. This system was also used to meter niobium pentachloride for a limited number of experimental runs. Hafnium tetrachloride and niobium pentachloride were metered with the powder feed mechanism also described earlier.

Tantalum Carbide

The development of an improved metering and injector system was conducted with tantalum pentachloride as the halide source material. The methane used was metered with a standard flowmeter. During this investigation 30 experimental runs were made initially which produced tantalum carbide on flat plate specimens. Standard graphite was employed as a substrate material.

Process conditions were investigated as well as the geometric arrangement in the deposition area. For example, injector tube sizes were varied from 1/8" diameter to 1/4" diameter, and injector distances from the hot zone varied from 1/2" to 6". The larger injector size was chosen because of its better performance. Small hole injectors eject gases at high velocities and often produced abnormal carbide growth rates in localized areas. The velocity of source gases does affect the uniformity of the coating but the velocity range required depends on the diameter of the mandrel to be coated. Varying the injector distance displaces the coated area as may be expected.

The deposition temperatures investigated were 2000°C and 2100°C. Below these temperatures lower deposition rates were obtained.

The deposition pressure was varied from less than 1 mm of mercury to 390 mm. At the higher pressures a great deal of soot was formed. To avoid soot formation pressures below 20 mm were maintained.

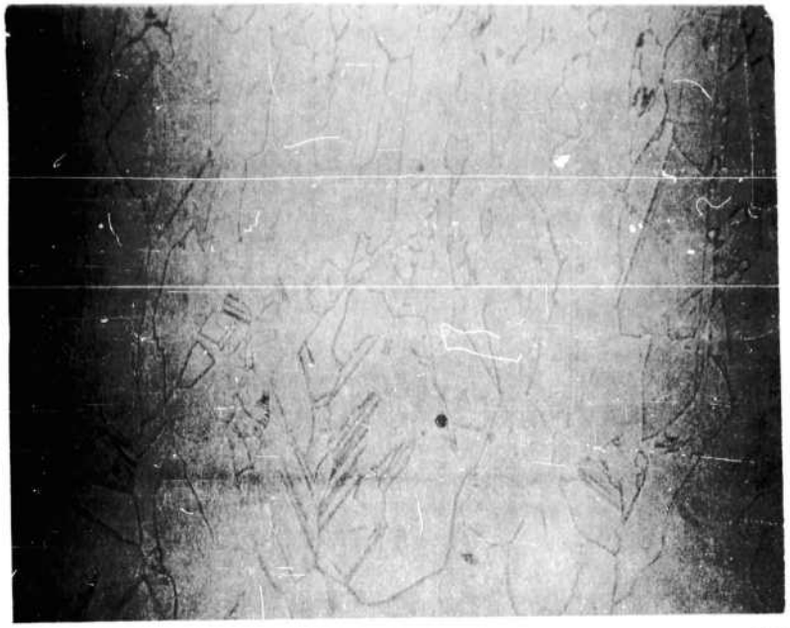
The deposition rate of tantalum carbide was found to be as high as 20 mils per hour. This is a maximum localized rate since perfectly uniform coatings were not obtained during this series of experiments. However, thin coatings in the range of a few mils were normally uniform.

A typical microstructure of tantalum carbide is shown in figure 15. This carbide is the well known gold colored carbide described as TaC. Deposited carbides normally have elongated grains which are perpendicular to the deposition surface and in the case of tantalum carbide twin lines are found in the structure. The degree of twinning is a function of the composition of the carbide. Figure 16 shows a multi-layered coating produced with different source gas ratios. The bottom layer in the photograph is one containing a metal concentration greater than the stoichiometric value for TaC. As this composition changes the degree of twinning also changes and few twin lines are found in a carbide of TaC composition.

The above investigation did not solve all technical problems. The coatings produced were not crack free, not perfectly uniform and abnormal carbide growths developed on injectors which were reduced only by retracting the injector from the deposition area. The need for evaluation samples in the forms of carbide coated test nozzle inserts led to an initiation of the nozzle coating phase of the program.

The development of tantalum carbide coated nozzles was carried out with a total of 152 experimental runs performed over a period of seven months. The following areas were investigated.

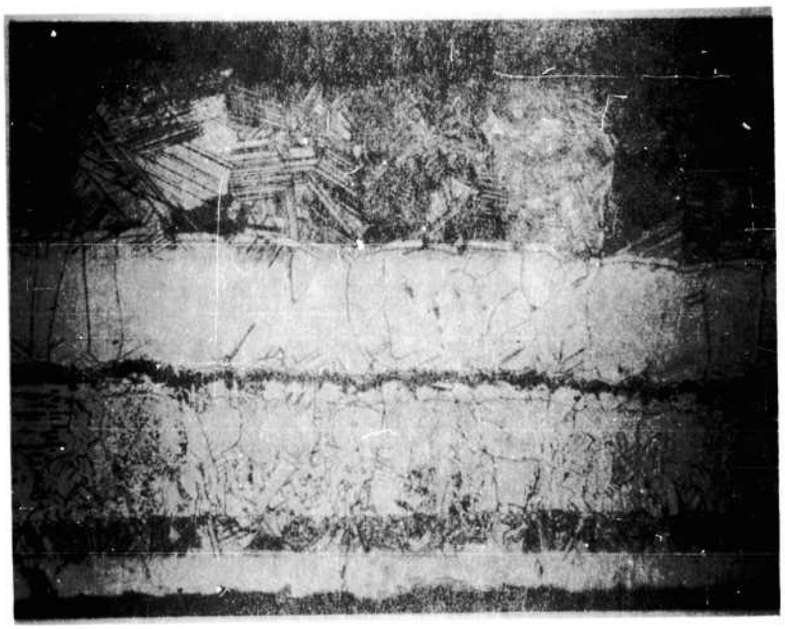
1. Substrate preparation for control of grain size of carbide deposits.



Tantalum Carbide — 200 X

Unpolarized — Etched

Figure 15



Tantalum Carbide — 100 X

Unpolarized — Etched

Figure 16

2. Flow rate of the source gases to obtain uniform carbide coatings.
3. Injector to nozzle distance for coating uniformity.
4. The use of baffle plates and nozzle jigging arrangement for uniformity of coatings.
5. Reversal coating of nozzles.
6. Injector positioning to prevent abnormal carbide growths on injectors.
7. Injector positioning to prevent abnormal carbide growths on the nozzle surface.
8. Injector design study.
9. Coating thickness required to prevent cracking of the carbide layer.
10. Investigation of graphite substrates.

The substrate preparation relates to the degree of polish of the surface and to the use of graphite suspensions to fill up voids in the surface. The better the polish, usually, the smoother the surface of the deposited carbide. However, the finer grained graphites produced the better surfaces. The use of graphite suspensions such as "aquadag" produced a weaker bond between the carbide and its substrate.

The flow rate of the source gas, injector to nozzle distance and the use of baffle plates are all related variables which are determined for a particular geometric arrangement. The baffle

plates which were rings of different internal diameter from 1/2" to 1-1/2" diameter were used below and sometimes above the nozzles for pressure control and to obtain a desirable flow pattern. The most common arrangement used was a baffle below the nozzle of a diameter equal to the throat diameter of the nozzle.

The nozzle jigging arrangement and the reversal coating of nozzles refers to the type of jigging required to obtain coatings only on the inner nozzle surface, and to the direction of flow for best coating uniformity. The nozzles, which have an outside taper, were positioned in a tube with a similar taper with their entrance edges left without backing for approximately 1/8 inch. The nozzles could then be coated and removed from their jigging without cracking the coating on the edge of the entrance cone. Most nozzles were coated with the source gases flowing over the entrance cone section first. With the source gases flowing through from the exit cone sections, only thin coatings could be produced over the edges of the entrance section.

The position of the injector in relation to the nozzle was a most critical factor. With injector distances less than 2" to 3" from the nozzle abnormal growths on injectors could not be avoided and simultaneously impingement growths on the nozzle surface would form. It was found that surfaces nearly perpendicular to the gas flow direction are difficult to coat with tantalum carbide without some localized areas having a greater coating thickness. The above phenomena were reduced by placing the

injector further from the nozzle, but in this case the coating rate on the nozzle was reduced because of loss of material which is deposited on jigging components between the injector and the nozzle. Because of this, injector distances were not greater than 6". Increasing gas flow velocities produced greater deposition rates on the nozzles but with the accompanying danger of producing abnormal growths on nozzle surfaces.

The relatively short injector design study made proved very beneficial. The abnormal carbide growths on injector tips which could not be avoided resulted in closing down the exit area of the injector. As the area decreased higher exit gas velocities were produced which led to abnormal growths on nozzle surfaces. The design study progressed from the construction of injectors with highly polished surfaces to injectors with bell shaped exhaust configurations. The bell shape is that which may be obtained by flaring the end of a piece of tubing. The above changes did not improve injector performance.

Injectors containing an additional concentric tube between the central heater section and the water cooled section were next investigated. A flow of argon gas which served as an inert gas blanket at the tip of the injector flowed through this concentric opening and reduced aspiration effects caused by effluent source gases. This type of injector, which greatly reduced injector growths, performed without any appreciable change in the injector

exit area. These units were used during the last few months of the program.

A great number of nozzles were found to have circumferentially cracked coatings at the throat and in many cases at the entrance section of the nozzles. The graphite substrates used and tantalum carbide have different coefficients of thermal expansion which cause stresses in the material on cool down from process temperature. The magnitude of the difference in coefficients is greater than two to one. Fewer cracks were found as the coating thickness increased and it was expected, initially, that coating thicknesses in the range of 40 to 50 mils would suffice. It was found, however, that coatings in this thickness range were also cracked.

Graphites with higher thermal expansion coefficients were investigated. Some of these graphites are special grades which are being produced on a small scale by graphite manufacturers. The highest coefficient obtained in graphites at the present time is in the range of 4 to 5 in/in/^{o}C, a value below the coefficient of tantalum carbide. Cracked coatings were also produced on these special graphites.

In order to produce sound coatings on test nozzles, which were required for evaluation, a lampblack base material with a thermal expansion coefficient of approximately 6 in/in/^{o}C was investigated. Sound coatings were produced on this material and prepared nozzles were submitted for evaluation. All of the carbide coated nozzles

Figure 17 **TaC Coated Test Nozzle**

which were tested will be discussed in a separate section. Figure 17 shows an ARC test nozzle insert coated with tantalum carbide.

Hafnium Carbide

The deposition of hafnium carbide was carried out in the second resistance furnace which in this case contained a 3" I.D. element. From preliminary experiments it was determined that the Hafnium tetrachloride source material could not be metered with the hot flowmeter system used for the metering of tantalum pentachloride. With hafnium tetrachloride, a thin residue was formed on the surface of glass which rendered a flowmeter inoperative.

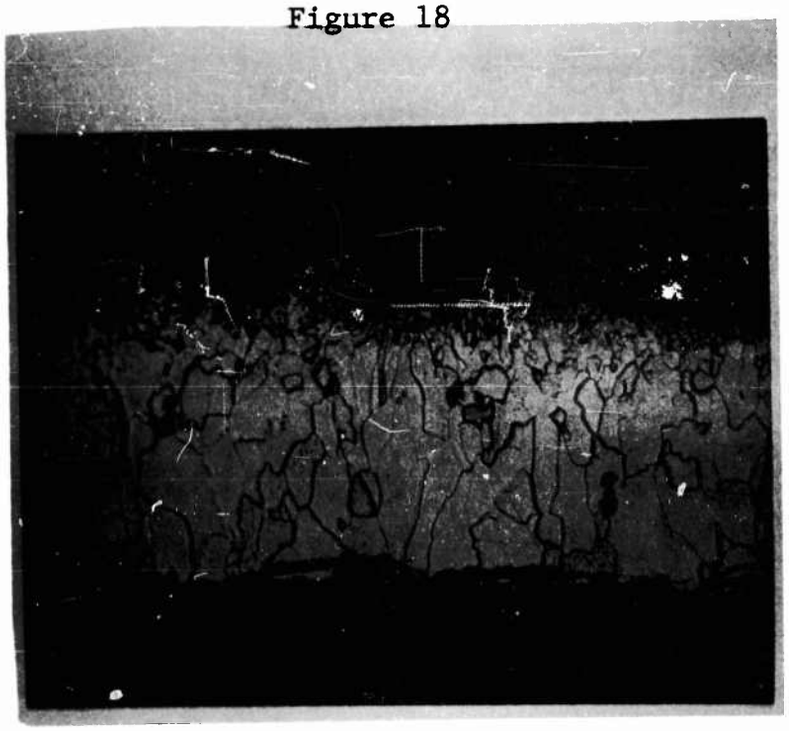
The system previously described which meters powdered halide from a hopper to an evaporator was developed for use with hafnium tetrachloride. The investigation of the deposition of hafnium carbide onto flat plates was limited initially to six experimental runs prior to the coating of test nozzle inserts. A deposition temperature of 2000°C was used throughout with a system pressure of less than 1 mm of mercury. The maximum deposition rate of hafnium carbide which was obtained was approximately 20 mils per hour, a value close to that obtained for tantalum carbide. This value for the deposition rate in no way presents the maximum rate obtainable nor the optimum rate which should be employed.

A typical microstructure of hafnium carbide is shown in figure 18. The crystal structure is seen to be columnar with the

Hafnium Carbide — 100 X

Unpolarized — Etched

Figure 18



Hafnium Carbide — 200 X

Unpolarized — Etched

Figure 19

axis of the grains perpendicular to the deposition surface. Figures 19 and 20 are also hafnium carbide structures produced under different sets of conditions. One structure is extremely fine grained and highly columnar while the other coarser and nearly equiaxed. The processing conditions for producing these structures cannot be given in terms of one set of operating conditions. It is believed that gas flow velocity, pressure, and source gas concentrations all play a role but that one of the variables is more influential than the others.

Source gas concentrations, as previously reported, play a very influential role in determining the number of phases present. Figures 21, 22, and 23 show the effects of increased concentrations of methane in the source gas. The percent carbide in a carbon matrix is seen to decrease to the point where a pyrolytic graphite structure is produced which contains a fine dispersion of carbides.

The development of hafnium carbide coated nozzles was initiated during the development of tantalum carbide coated nozzles. The investigation for the coating of sound, crack-free, hafnium carbide nozzles required 28 experimental runs. The process variables and the factors involved in coating test nozzles with HfC were the same as described for the development of TaC coatings.

Hafnium carbide coatings produced on normal graphite contained cracks even in thicknesses up to 70 mils. With the lampblack based graphite crack-free coatings were produced in thicknesses of 10 to 44 mils. Figure 24 shows three ARC nozzles coated with hafnium

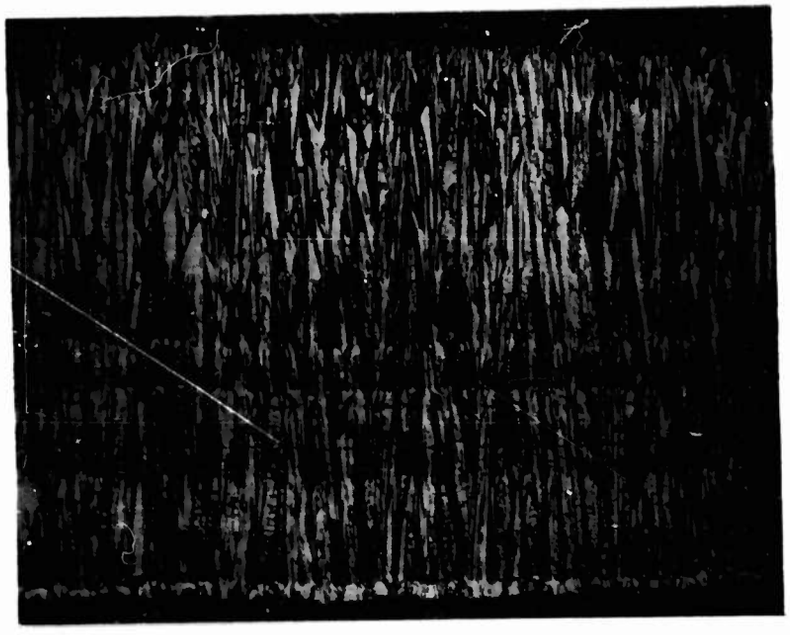
Hafnium Carbide

Unpolarized

100 X

Etched

Figure 20



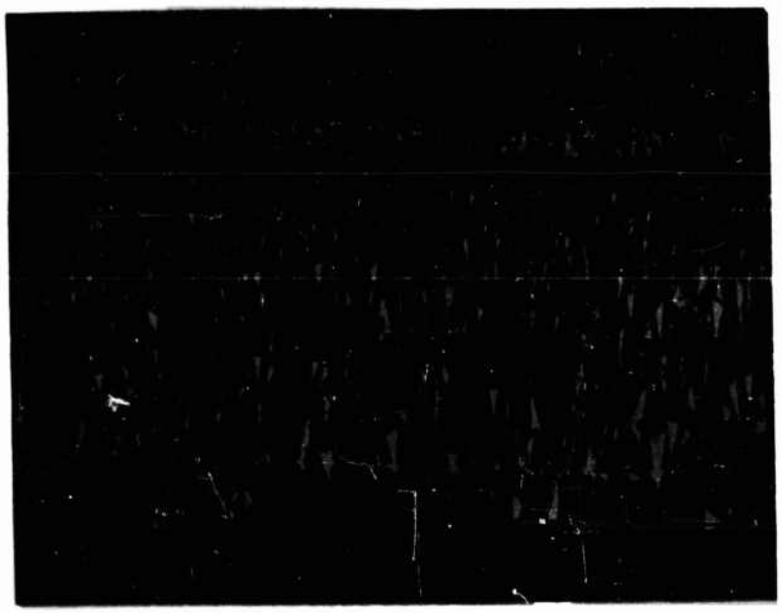
Hafnium Carbide + Carbon

Unpolarized

100 X

Etched

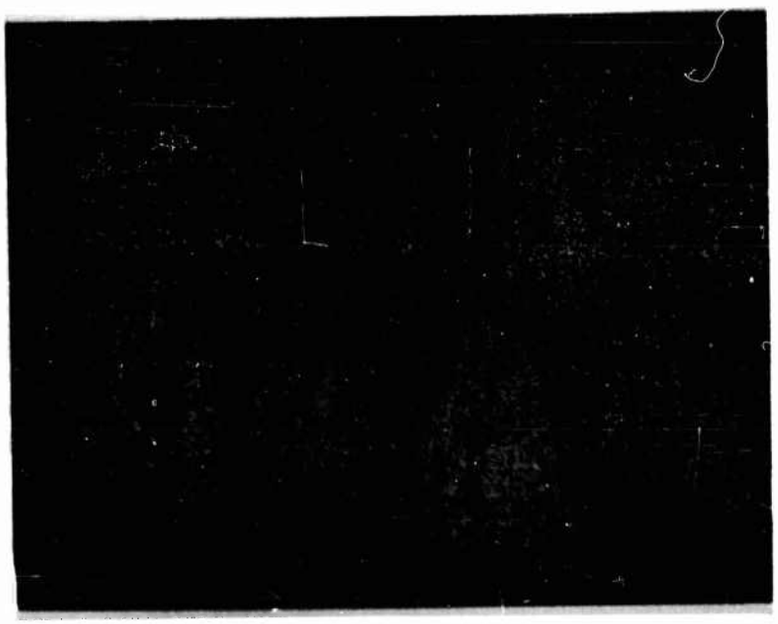
Figure 21



HfC + Graphite 100 X

Unpolarized

Figure 22



Pyrolytic Graphite + HfC 100 X

Unpolarized Etched

Figure 23

Figure 24 HfC Coated Test Nozzles

carbide. The two light colored nozzles still have on their surfaces the dye penetrant and developer which was used to show cracks. The completely crazed or cracked carbide was produced, in this case, on ATJ graphite. The darker metallic nozzle has a 10 mil coating which was also found to be completely crack free. These results show, therefore, the feasibility of producing relatively thin crack-free hafnium carbide coatings.

Niobium Carbide

The development of niobium carbide coatings was accomplished in the same resistance furnace used for the development of hafnium carbide coatings. The metering system used was the powder feed system which was developed for the metering of hafnium hexachloride.

Using previously established operating conditions four process runs were made to produce coatings onto flat plates. The microstructure of the niobium carbide produced is similar to the microstructure previously shown; however, one coarse grained structure obtained may be of interest. Figure 25 shows the niobium carbide coating, in contact with its substrate. The lower boundary line in the figure represents the carbide-graphite interface and shows that no interaction takes place between the two materials.

The niobium carbide nozzle coating phase of the program was accomplished with 33 process runs. Coatings from 5 mils to 40 mils were produced and irrespective of coating thickness cracked coatings were produced on normal graphite grades, such as the ATJ

grades. The sound coatings produced for evaluation were produced on the lampblack base material. Figure 26 shows an as-deposited niobium carbide coated ARC nozzle.

Niobium Carbide on Graphite — 200 X

Unpolarized — Etched

Figure 25

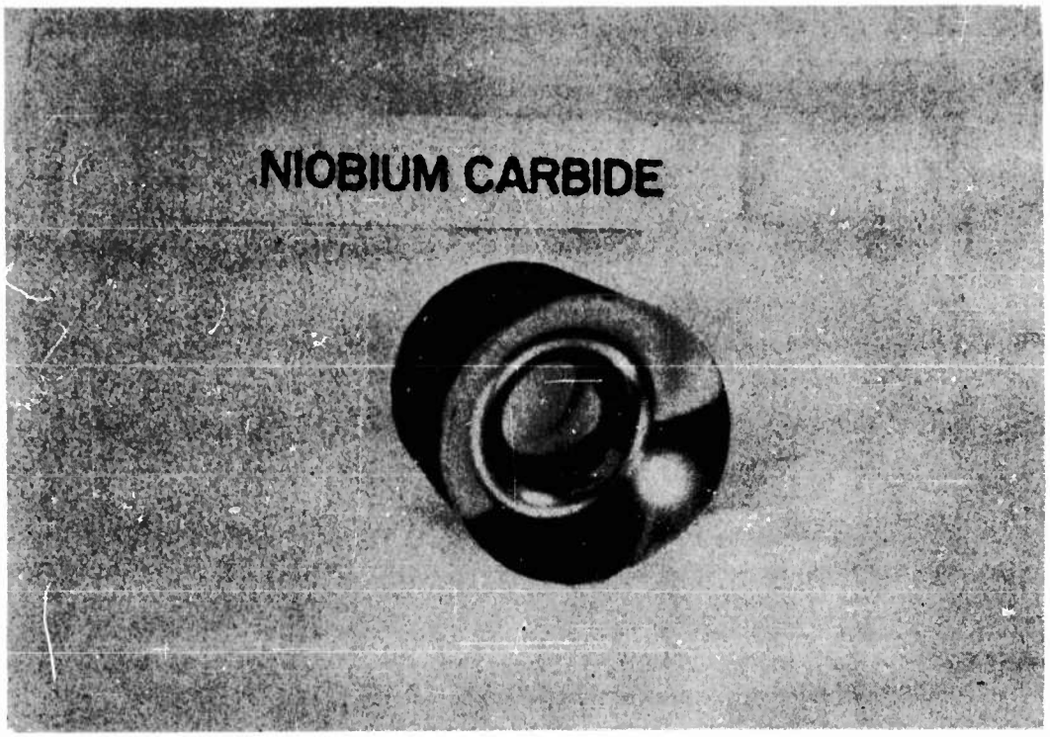


Figure 26 NbC Coated Test Nozzle

CARBIDE COATING OF FULL SCALE NOZZLES

The carbide coating of full scale Polaris nozzles was carried out in the modified resistance furnace previously described. A separate halide metering system which consisted of a powder feed mechanism of the type already described was used for metering tantalum pentachloride and niobium pentachloride.

A first series of 14 process runs was made for the development of tantalum carbide coatings.

The first experimental runs were made to determine the flow conditions necessary for coating full scale nozzles. It was found that injector growths were formed at a faster rate in a large system and that these growths were the direct cause of impingement growths on the surface of a nozzle. The increased exit source gas velocity which results as the exit hole of the injector becomes smaller produced two adverse effects. One, the coated area which was subject to the higher source gas velocity was normally metal rich; and two, this area grew in thickness at a faster rate than the remaining carbide coating. The injector growths could be blown off during operation but a carbide of uniform thickness and composition could not be produced by this practice. Injector growths rates were markedly reduced by aniaspiration sleeves around the injector and by retracting the injector from the high temperature deposition area.

During the above investigation two symmetric nozzles were coated with tantalum carbide. The coatings were uniform but a deposition rate of only approximately 1 mil per hour was obtained. One of the TaC coated nozzles along side on ARC test nozzle is shown in figure 27. The coating thickness of few mils appeared to be adherent to the substrate but was found to be cracked or crazed. The only substrate material available at this time in the size required was ATJ graphite and other more common grades.

A series of 18 experimental runs were made to investigate the niobium carbide coating of full scale nozzles. A number of process runs produced either no deposit or pink black sooty deposits which were probably caused by leaks in the system. On a few occasions leaks have developed only during a process run.

One unavoidable delay was encountered during this phase of the program which seriously affected the expected results. The lampblack base graphite which was required to produce crack-free coatings was not available in sizes sufficiently large for the machining of full scale nozzles. Attempts were made to bond pieces together with graphite adhesives but these were not successful. Toward the end of the contracting period blocks of material which were produced specifically for this application were received. An attempt was subsequently made to demonstrate the feasibility of producing sound carbide coatings on full scale hardware. Figure 28 shows two nozzles which were coated with thin coatings of niobium carbide and tantalum carbide. The mandrel or

substrate material was reduced in thickness to a shell in order to reduce the thermal stresses caused by even a small mismatch in thermal expansion coefficients.

The above results demonstrate the feasibility of producing carbide coatings on full scale hardware, but the task of producing thick coatings in the 30 to 50 mil thickness range was not accomplished.

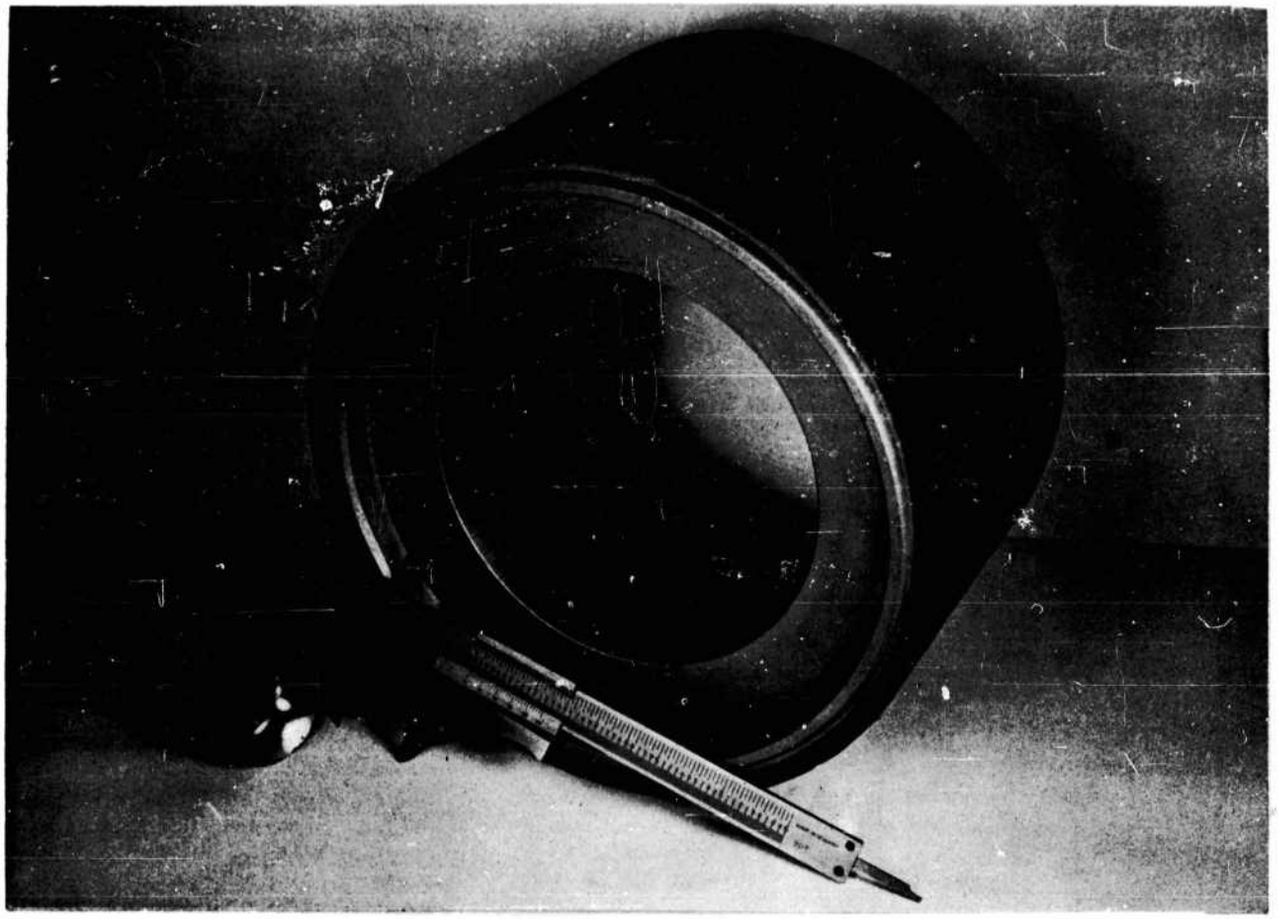


Figure 27 Tantalum Carbide Coated ARC and Full Scale Nozzle

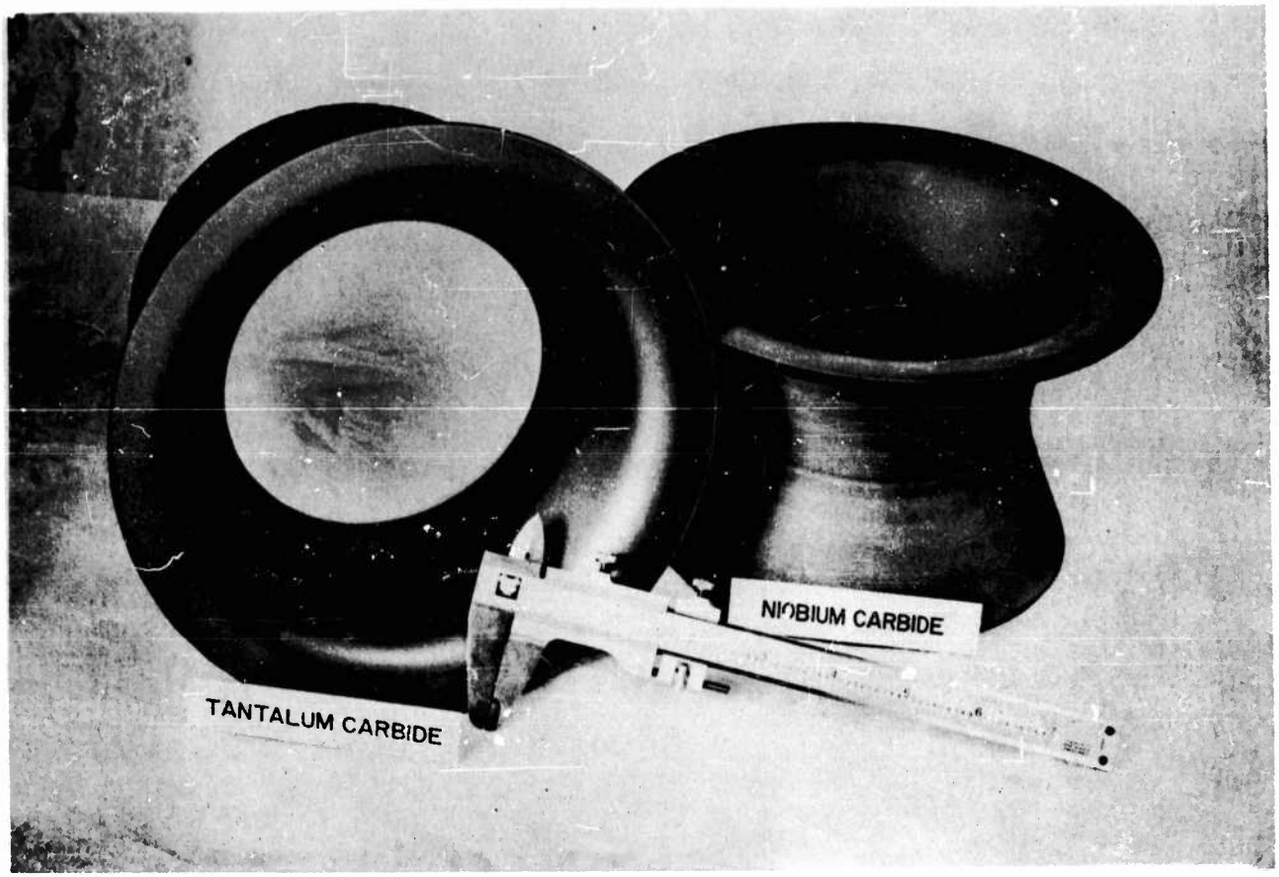


Figure 28 **Carbide Coated Full Scale Nozzles**

MATERIALS EVALUATION

Initially the development of pyrolytic silicon carbide was investigated with the aim of establishing a model processing scheme applicable to the processing of other carbides. Because of the high vapor pressure of silicon carbide at pyrolytic process temperatures, the development work on this material was found to be of limited value. The silicon carbide produced pyrolytically was β silicon carbide. The only property measured was the microhardness of the material. The average knoop number with a 100 grain load for silicon carbide was found to be 2509. In comparison, commercial silicon carbide is reported to have a knoop microhardness of 2550.

The three carbides produced pyrolytically, namely TaC, HfC, and NbC, have similar characteristics as may be seen from X-ray diffraction analyses.

a) Crystal Structure

The carbides TaC, HfC, and NbC all have a face centered cubic lattice where the smaller carbon atoms are located interstitially in a structure of the NaCl type.

b) Lattice Parameters

The lattice parameters of pyrolytic carbides are listed in the following table along with values reported in the literature or measured with commercial powders.

Carbide	Lattice Parameter A
Tantalum Carbide	4.418 -- 4.429
TaC Powder	4.453
Niobium Carbide	4.464 -- 4.466
NbC Literature	4.42 -- 4.47
Hafnium Carbide	4.629
HfC Literature	4.63 -- 4.70

A difference is seen in the case of tantalum carbide where the pyrolytic carbide has a smaller lattice parameter. In comparison pyrolytic NbC has a somewhat larger lattice parameter than some reported values, but the values obtained are in the same range. The lattice parameter of pyrolytic hafnium carbide may be said to be also in the range of the reported values.

The lattice parameter of a carbide should be related to its carbon content over a certain composition range. The pyrolytic process offers the means of controlling the carbon content of a carbide since the composition of the material produced is related to the ratio of the constituents in the gas phase.

c) Crystallite Size

By X-ray diffraction a measure of the crystallite size was obtained from the half intensity breaths of the (200) (111) and (220) peaks. The crystallite size L(hkl) obtained from these peaks is equal to the average depth of coherently diffracting layers perpendicular to the surface. For example, $L_{(111)}$ is the average depth perpendicular to the surface of coherently diffracting

domains having their (111) planes parallel to the deposition surface. The crystallite sizes of the pyrolytic carbides along with the values for commercial carbide powders are listed in the following table. In some cases the peaks were of such low intensity that no crystallite size value could be obtained.

	Crystallite Size A		
Carbide	$L_{(200)}$	$L_{(111)}$	$L_{(220)}$
Tantalum Carbide	465	350	500
Tantalum Carbide	354	235	730
TaC Powder	465	510	500
Niobium Carbide	315	170	
Niobium Carbide	2500		
NbC Powder	315	730	72,500
Hafnium Carbide	455	410	248

The values for the same carbide show the difference which is obtained between samples.

Preferred Orientation

A pronounced texture or a strong tendency for certain crystal planes to align themselves parallel to the deposition surface was found in all of the carbides produced pyrolytically. The procedure used to measure the preferred orientation is to compare the intensity of a particular reflection with those of other reflections, since the relative intensities will be a function of the degree of preferred orientation. The intensity ratios for a random sample

may be calculated and used to normalize the measured intensity ratios to give a number called the texture index. The results obtained are listed in the following table.

Carbide	$N_{(200)}/N_{(111)}$	$N_{(200)}/N_{(220)}$
Tantalum Carbide	631/8	610/12
Tantalum Carbide	9,120/8	2020/12
TaC Random	6/8	6/12
Niobium Carbide	530/8	42,000/12
Niobium Carbide	7200/8	20,500/12
NbC Random	6/8	6/12
Hafnium Carbide	$N_{(220)}/N_{(111)}$	$N_{(220)}/N_{(200)}$
HfC Random	32.7/8 12/8	420/6 12/6

From the above results it should be noticed that Tantalum Carbide and Niobium Carbide are deposited with the cube plane of the lattice parallel to the deposition surface. Hafnium carbide is deposited with many of its (110) lattice planes parallel to the deposition surface. The factors influencing the texture of deposited carbides are not known at the present time.

Other Properties

The microhardness test was found to be a relatively simple method for evaluating the carbides produced. In the case of tantalum carbide and niobium carbide as the carbon content of the carbides was reduced below the stoichiometric value the structures contained an increasing density of thermal twins. The microhardness

of the carbides also decreased as this twin density increased. From the microhardness surveys made throughout the program it was possible to grade the carbides produced in the following tables:

Carbides with a Metal to Carbon Ratio Near Unity

	K_{100}	K_{100} from literature
TaC	2100 - 2400	1800 - 1950
HfC	2200 - 2400	-------
NbC	2400 - 2700	2400 - 2470

Carbides High in Carbon (single phase)

	K_{100}
TaC	2400 - 3500
HfC	2400 - 3500
NbC	2700 - 4000

Carbides with lower microhardnesses were also produced but in this case two phases were sometimes present and hardness ranges for these carbides cannot be given.

The high hardness carbides which are seen to be considerably harder than reported values were found to be extremely brittle and difficult to handle. Those samples which could be prepared for bend test measurements were found to have bend strengths in the range from 10,000 to 40,000 psi. This range of bend strength may be used for all of the carbides. Higher bend strength values, as high as 150,000 for one TaC sample, were obtained; however, these

values cannot be representative of the carbides since they were metal rich in composition. The bend strength measurement of carbides is also subject to errors because of the difficulty in preparing samples without surface imperfections such as grinding checks. For example, the following bend strengths were measured for TaC: 11,150 psi, 16,410 psi, 23,024 psi, 38,400 psi and 46,300 psi.

Thermal Expansion

The thermal expansion coefficients of tantalum carbide and niobium carbide were measured; however, because only a few measurements were made, the data should be considered preliminary.

Thermal Expansion in/in/^{o}C

Temp.	NbC	TaC
600^{o}C	$5.90_{(10)}{}^{-6}$	$6.0_{(40)}{}^{-6}$

The thermal expansion coefficients of the above named carbides are in the same range as the lampblack base material used as substrate, and their compatibility in this respect is the reason why crack-free carbide coatings could be produced.

Oxidation Resistance

Oxidation tests were made in a simple zirconia combustion tube heated indirectly by induction. Dry air was used for the tests at a rate of one liter per minute. The velocity of the air stream which is an important quantity was set at a single value of 21 ft/min.

The oxidation resistance of tantalum carbide was measured initially by measuring the weight loss of samples after an oxide layer which formed on the material had been removed.

The oxidation rate in grams/in^2/hr. at different temperatures was determined and the results compared to results obtained with tantalum, tungsten and silicon carbide.

Material	900°C	1000°C	1200°C	1400°C
W	0.5426	0.5420	catastrophic oxidation	
Ta	Catastrophic at all temperatures			
SiC	0.0020	0.0037	0.0097	0.0142
TaC	0.2490	1.08	3.76	13.45

On a relative basis it is seen that the oxidation rate of tantalum carbide is much greater than that of silicon carbide, but that tantalum carbide is a great deal more oxidation resistant than tantalum above 900°C and superior to tungsten above 1200°C. The oxidation rates of the three carbides were measured in a separate series of experiments where measurements of the weight differences before and after the tests were made. On a comparison basis it was found that at approximately 1100°C the oxidation rate of TaC changed from positive to negative. For NbC and HfC this transition temperature is lowered approximately 100°C but an exact temperature difference was not obtained. The scatter in the data obtained forbids the presentation of oxidation curves; but for the sake of comparison, the temperatures at which a weight loss of approximately

0.01 gms/cm^2/min were obtained were 1250°C for TaC, 1125°C for NbC and approximately 1025°C for HfC. The oxidation rates of the carbides were increased approximately threefold over the above rate with a temperature increase of 200°C.

The evaluation of pyrolytic carbides in thermal shock and erosion resistance was determined by nozzle insert tests conducted at the Atlantic Research Corporation. Since pyrolytic carbides were developed primarily for application to rocket nozzles, the development of coated test nozzles was of prime importance during the course of this program. The following table presents in brief the number of nozzles tested and the results obtained. The propellant temperatures for all tests were in the region of 5600°F.

Carbide	Coating Thickness	$P_{max.}$	Powerage	Results
HfC	35 mils	955	442	Coating removed in 5 sec.
HfC	48 mils	---	---	Motor malfunction
TaC	2-5 mils	---	---	Motor malfunction
TaC	18 mils	1070	952	Coating removed in 5-6 sec.
TaC	23 mils	941	723	36 sec. firing; no measurable erosion of coating at throat
NbC	10.5 mils	706	634	41.8 sec. firing; no measurable erosion of coating at throat
NbC	5 mils	914	795	29 sec. firing; some coating left at throat

The hafnium carbide coating tested was the first carbide coated nozzle tested. Its approximate five second life before fracture indicates that thermal shock may be the cause of failure. However, in view of the fact that only one tantalum carbide coated nozzle failed in this fashion, one may speculate that the mode of failure was associated with some other weakness in the nozzle systems.

Two post fired nozzles, a tantalum carbide coated nozzle and a niobium carbide coated nozzle, are shown in figure 29. In both nozzles damage in terms of coating removal took place in the exit cone sections. The niobium carbide was retained over the entire entrance section and over most of the throat section. The same results were obtained with the tantalum carbide coating except that in this case only approximately two thirds of the coating was removed from the exit section. The adhesion of both coatings after firing appeared to be excellent. Throat area changes were measured which did not indicate the amount of erosion of the carbide coatings. For example, the 23 mil TaC coated nozzle changed from .559 to approximately .574 while the thickness of the coating did not change. The NbC carbide coatings also survived the tests without any change in coating thickness at the throat section. The area change measured may have been caused by creep of the substrate at elevated temperatures.

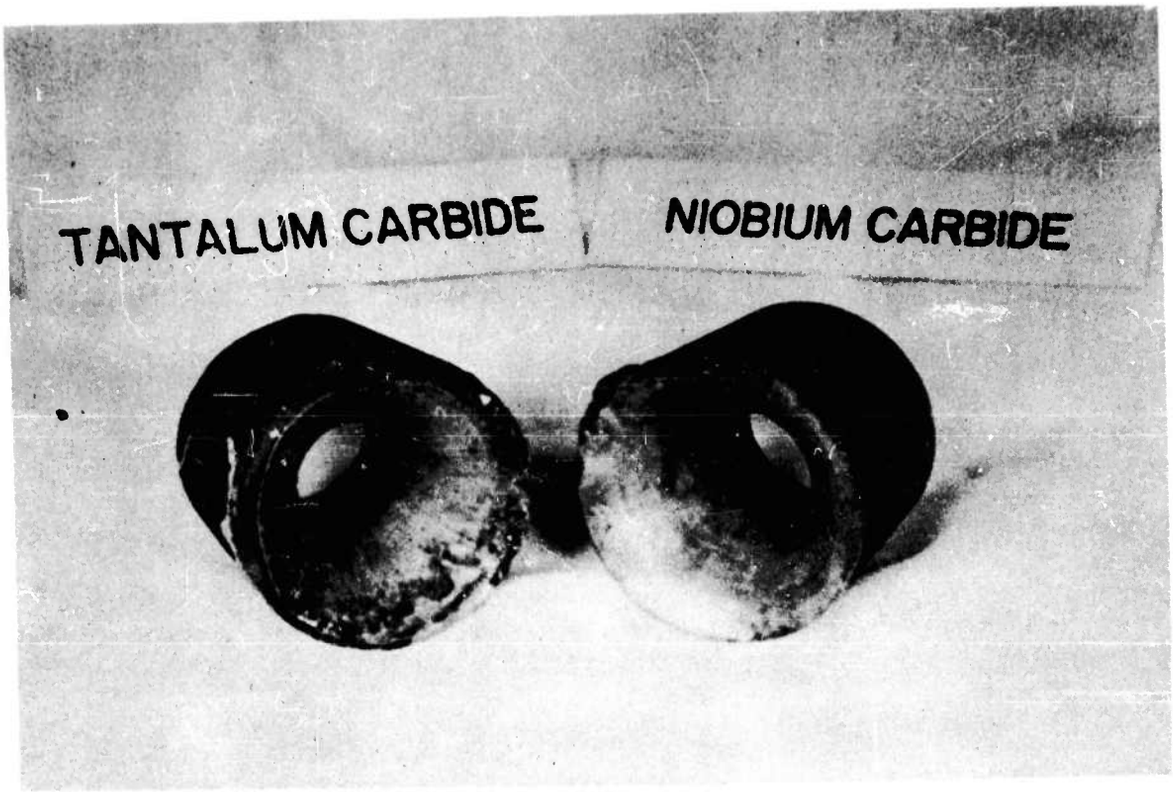


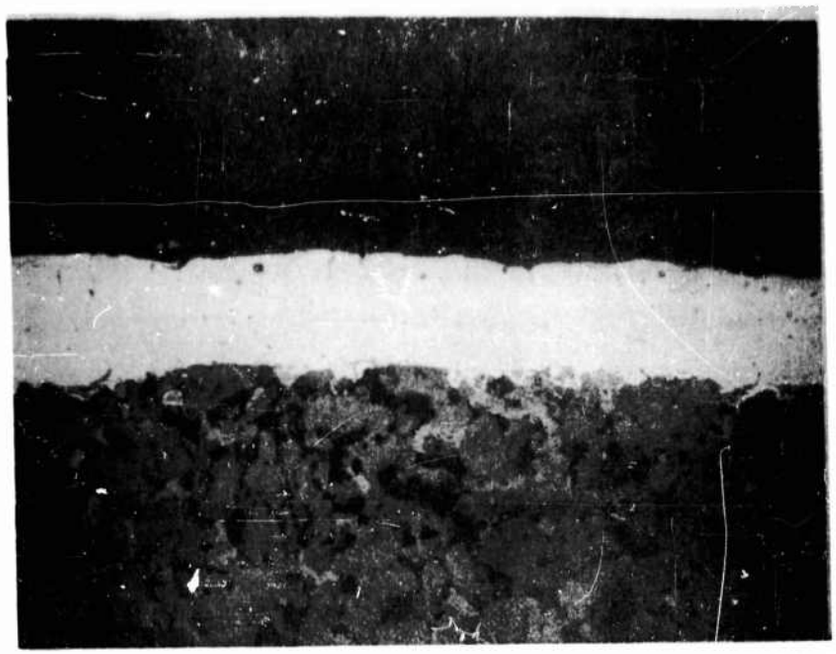
Figure 29 Coated Test Nozzles After Firing in 5600°F Propellant

The firings also caused cracks in the coatings which ran from the entrance cone through the throat section. Since the cracks were only fine surface lines, their formation probably took place on cooling after the test.

The type of failure which did take place does not appear to have resulted from either erosion or melting of the coating but appears to result from thermal stresses. It is also possible that gases were evolved from the substrate during the test which caused the exit cone failures.

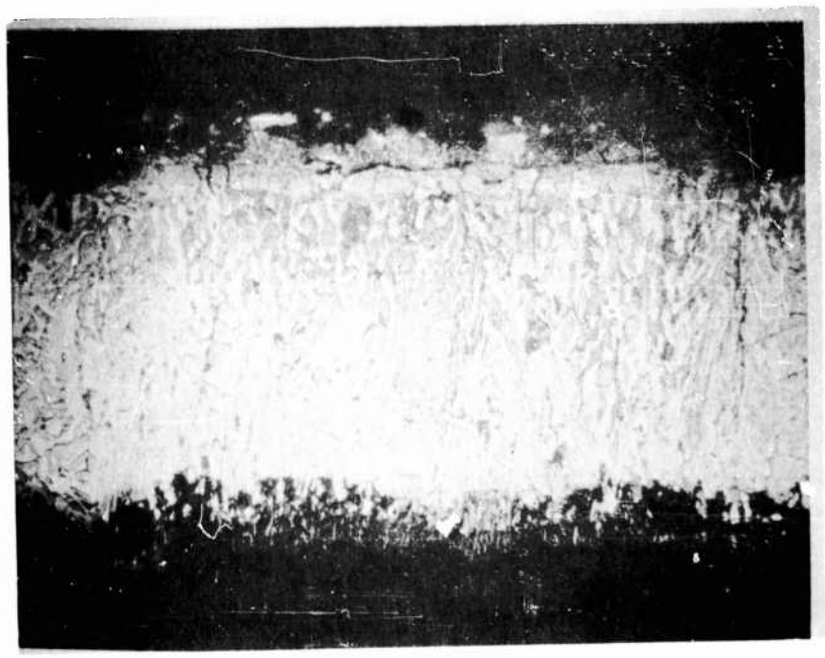
Sections of the coated nozzles were taken subsequent to the firings. Figure 30 shows a section of a post fired NbC coated nozzle. The adhesion of the coating which was obtained by interlocking of the coating to the substrate was retained and little or no change appears to have taken place in the coating itself. One change was observed in the substrate for a depth of approximately one eighth inch next to the coating. A dispersion of a second phase in the substrate which appears to be a graphitization of part of the material was caused by the firing. There may be associated effects from the above change in structure.

Figure 31 shows a section of the post fired TaC coated nozzle. The same change in the structure of the substrate was observed and in addition there appears to be a leaching of tantalum on the exposed surface. The observed change in the tantalum carbide coating does not appear to be the cause of the partial failure obtained, but it may be a contributing factor.



Niobium Carbide Coating After Firing 100 X

Figure 30



Tantalum Carbide Coating After Firing 100 X

Figure 31

CONCLUSIONS

The improvement in rocket nozzles performance in terms of very low erosion rates which may be gained by the use of refractory carbides as surface coatings was not conclusively shown. Tests performed with a 5600°F propellant revealed that the erosion of carbides is negligible but that technical problems require solutions before the materials can be used. It is believed that the partial failures obtained were caused by thermal stresses and not by thermal shock. As thin, well bonded layers on a graphite substrate, the costings would only serve as an erosion resistant barrier and the thermal stresses developed during firing would then be sustained by the graphite backup.

The adhesion of the carbides to graphite was satisfactory so long as the thermal coefficients of the carbide and its substrate were fairly close. The adhesion of coatings may be further improved with special surface preparations.

A number of graphites with thermal coefficients of expansion in the range of 4 to 4.5/°C have been developed. Graphite manufacturers expect that coefficients can be increased to the range of the coefficients of carbides. In the meantime, the use of thin mandrel back up may provide a solution or lampblack based graphites may be used.

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